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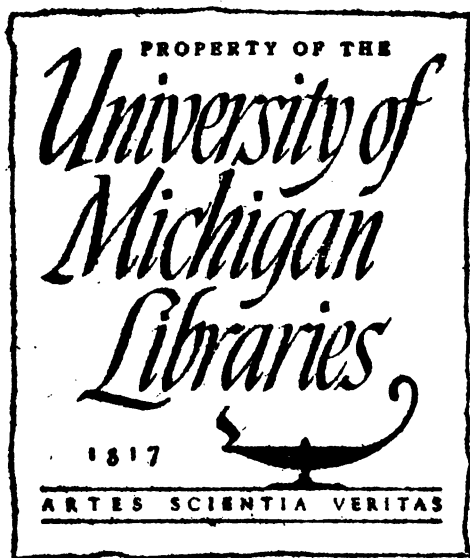
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JOURNAL

OF

THE CHEMICAL SOCIETY.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*On the Volumetric Estimation of Bismuth in the Form of Oxalate.*

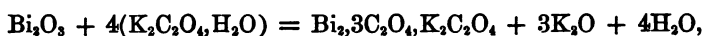
By M. M. PATTISON MUIR, M.A., F.R.S.E., Fellow and Prælector in Chemistry, and C. E. ROBBS, B.A., B.Sc., Scholar, of Gonville and Caius College, Cambridge.

1. A process for estimating bismuth by precipitation as neutral oxalate, and conversion of this into acid oxalate, by washing with boiling water, was described by one of us in this Journal (1878, Trans., 70). This process involves boiling the precipitated oxalate for some little time with successive quantities of water, collection of the acid oxalate, and complete washing of the same, and solution in acid, before titration with permanganate.

In the *Berichte* (14, 1172) a method is described by von Reis for gravimetrically determining various heavy metals, based on the precipitation of oxalates of these metals by addition of potassium oxalate to solutions in acetic acid. It is there shown that when normal potassium oxalate is added to a solution of bismuth, nearly free from mineral acid but containing acetic acid, a double salt having the formula $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot \text{K}_2\text{C}_2\text{O}_4$ is precipitated. By collecting and washing this precipitate, burning it with ammonium nitrate, and washing out potassium salts, pure bismuthous oxide is obtained.

The formation of this double oxalate seemed a reaction very suited to be the foundation of a volumetric process for determining bismuth. If bismuth can be completely precipitated by normal potassium oxalate, and if the precipitate is fairly stable, it seemed probable that the amount of bismuth in a solution could be determined by adding a known quantity of a standardised solution of the oxalate, precipitating in a graduated flask, drawing off an aliquot portion of the supernatant liquid, and titrating with permanganate.

2. According to the equation—



117 parts of bismuthous oxide require 184.2 parts of crystallised normal potassium oxalate for complete precipitation.

In the first series of experiments we used a solution of bismuthous oxide in hydrochloric acid; measured quantities of this were evaporated nearly to dryness on a water-bath, the residues were dissolved in glacial acetic acid, the liquids transferred to graduated flasks, and measured quantities of a solution of pure normal potassium oxalate of known strength were added: after standing for some time the nearly clear supernatant liquids were filtered through dry filters into dry beakers, and oxalic acid was determined in aliquot portions of the filtrates by titration with standardised permanganate.

Many experiments were conducted with varying relative quantities of bismuth and potassium oxalate; in some cases a little water was used along with glacial acetic acid to wash the liquids into the measuring flask, in other cases glacial acetic acid alone was employed; the results varied, but in many trials made under similar conditions we obtained from 97 to 98.5, and in one instance 100.3 per cent. of the bismuth known to be present.

When a great excess of potassium oxalate was used, the result was invariably low, unless a large quantity of glacial acetic acid was added; the double oxalate of bismuth and potassium is soluble in an excess of potassium oxalate, but is reprecipitated by addition of much strong acetic acid.

A difficulty was generally experienced in dissolving the bismuth chloride obtained by evaporating the solution in acetic acid; when the evaporation was carried to complete dryness, a small quantity of a salt—most probably bismuthyl chloride—was formed, which refused to dissolve in acetic acid; when a little hydrochloric acid remained, the results showed somewhat marked variations.

3. A second series of experiments was conducted with the same solution of bismuthous oxide, but the residue obtained on evaporation was dissolved in nitric acid and again evaporated nearly to dryness, before solution in acetic acid: much more concordant results were thus obtained. We quote two:

gram. Bi_2O_3 used.	gram. $\text{K}_2\text{C}_2\text{O}_4, \text{H}_2\text{O}$ added.*	gram. $\text{K}_2\text{C}_2\text{O}_4, \text{H}_2\text{O}$ found in solution.	gram. $\text{K}_2\text{C}_2\text{O}_4, \text{H}_2\text{O}$ used.	gram. Bi_2O_3 found.	Percentage Bi_2O_3 found.
0.3349	0.5999	0.0749	0.5250	0.3335	99.59
0.3349	0.5999	0.0747	0.5252	0.3336	99.61

* This salt is said sometimes to crystallise with 2 mols. of water: the salt we used was prepared by neutralising the acid oxalate with potassium carbonate, crystal-

4. A solution of bismuthous oxide in the minimum quantity of nitric acid was now prepared, and a series of determinations made by evaporating off the greater part of the free acid, always, however, allowing acid to remain sufficient to keep the bismuth in solution when the liquid was hot; adding a large excess of glacial acetic acid; transferring to a measuring flask; washing in the liquid with acetic acid (1 : 1); adding about twice as much potassium oxalate, in aqueous solution, as there was bismuthous oxide present; making up to the mark with acetic acid (1 : 1); and, after shaking and standing for some time, filtering through a dry filter, and determining residual oxalate by titration with permanganate.

The results were satisfactory. We give instances.

gram. Bi ₂ O ₃ taken.	gram. K ₂ C ₂ O ₄ .H ₂ O added.	gram. K ₂ C ₂ O ₄ .H ₂ O found in solution.	gram. K ₂ C ₂ O ₄ .H ₂ O used.	gram. Bi ₂ O ₃ .	Percentage Bi ₂ O ₃ .
				Found.	
0.3268	0.5999	0.0949	0.5050	0.3208	98.20
0.3268	0.5999	0.0889	0.5110	0.3246	99.33
0.3268	0.5999	0.0857	0.5142	0.3267	99.97
0.3268	0.5999	0.0856	0.5143	0.3268	100.00
0.3268	0.5999	0.0858	0.5141	0.3266	99.95

5. In applying this process to the determination of bismuth in mixtures, it is necessary that the bismuth should be separated from other heavy metals—this may be done by precipitation as oxychloride—and that it should be obtained in solution as nitrate along with a small excess of nitric acid. Inasmuch as a large excess of potassium oxalate must be avoided, the standardised solution of this salt may be advantageously run from a burette into the measuring flask in small successive quantities; when precipitation is apparently complete, a few cubic centimeters of the solution are added, and the process continued as described in the preceding paragraph.

6. In one series of experiments we attempted to wash the double bismuth-potassium oxalate, dissolve the salt in acid and titrate with permanganate, but we found that the double salt, like normal bismuth oxalate, is slowly decomposed by cold and more rapidly by hot water, with solution of alkaline oxalate.

The method adopted by v. Reis for purifying the double oxalate is not described in the *Berichte*; other oxalates of heavy metals were, however, washed with a mixture of equal volumes of water, glacial acetic acid, and alcohol. We prepared a quantity of bismuth potassium oxalate, washed it with this mixture till the washings were free from alkaline oxalates, and dried it in a vacuum over sulphuric acid for lising from water, and drying between filter-paper; analysis showed the above formula to be correct.

some weeks. As thus prepared the salt gave numbers closely agreeing with the formula $\text{Bi}_2, 3\text{C}_2\text{O}_4, \text{K}_2\text{C}_2\text{O}_4$; it lost about 1 per cent. of its weight at 100° , but underwent no further loss at 160° ; decomposition began at about 170 — 180° . We therefore conclude that the formula given by v. Reis for this salt is correct, and that the salt, after drying in a vacuum over sulphuric acid, contains no water of crystallisation.

II.—*The Action of Water on Bismuthous Iodide: a Lecture Experiment.*

By M. M. PATTISON MUIR.

THE action of water on bismuthous iodide affords a reaction well adapted for illustrating the influence of (a) time; (b) temperature; (c) mass, on a chemical change. The experiment may be conducted in two ways, the second of which is, I think, perhaps the best: the meaning of the expressions "direct" and "reverse" action may also be well illustrated by this modification of the experiment.

A quantity of aqueous hydriodic acid—about 1 part strong acid to 100 parts water—is divided into two equal parts; one is heated to boiling, the other remains cold: a small quantity of the cold solution is diluted with about three times its own bulk of water; a little of this is again diluted with about three or four times its own bulk of water. The four liquids are placed in beakers standing on white surfaces, with white backgrounds, and a few grains of solid bismuthous oxide are shaken into each. In the cold comparatively concentrated liquid, brown BiI_3 is produced; in the hot liquid, red BiOI ; in the cold and moderately dilute, BiOI ; and in the most dilute there is little or no action. The brown BiI_3 slowly changes on standing to red BiOI .

The experiment may be conducted more easily and with more striking effect by pouring a little of a solution of BiI_3 in concentrated hydriodic acid into three beakers standing on white surfaces and with white backgrounds, and containing (1) a little cold water (about 100 c.c.); (2) the same quantity of water at about 90 — 100° ; (3) a large quantity (about 500 c.c.) of cold water. Brown BiI_3 is precipitated in (1); red crystalline BiOI in (2); and red BiOI , but in smaller quantity, in (3). Here again the brown BiI_3 is slowly changed to red BiOI on standing: by pouring a little strong hydriodic acid into this beaker after this change is nearly complete, the reverse change—with reproduction of brown BiI_3 —is rendered very apparent.

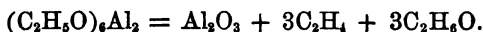
III.—*Aluminium Alcohols. Part II. Their Products of Decomposition by Heat.*

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.,
Lecturer on Chemistry in Dulwich College.

WE lately described some alcohols in which the basic hydrogen is replaced by aluminium (*Chem. Soc. J.*, 1876, p. 158; 1881, p. 1; *Proc. Roy. Soc.*, 1880, p. 546). We have also observed (*Proc. Roy. Soc.*, 1880, p. 548) that these compounds are decomposed by heat, and that in two ways: they may split up into alumina and the alcohol and olefine, or into alumina and the ether. The further investigation of this matter forms the subject of the present paper.

Ethyl Series.

The effect of heat on the aluminic ethylate has already been partially described. Although the compound may be distilled *in vacuo*, it is almost wholly broken up near its boiling point under the ordinary pressure of the atmosphere. A little ether is formed, but the decomposition takes place almost entirely into ethene, alcohol, and alumina, thus:—



In the case of the amylate, a similar decomposition occurs, but the yield of amylic ether is somewhat greater.

Phenyl Series.

If similar reactions take place with the aluminic alcohols of the phenyl series, we should obtain the simple ethers $(\text{C}_n\text{H}_{2n-7})_2\text{O}$, only one of which has been described, together with the hydrocarbons, C_6H_4 and C_7H_6 , and their homologues. We therefore studied more completely the action of heat upon the aluminium derivatives of certain of the phenyl alcohols.

Aluminium Phenylate.

469 grams of this compound were heated in a flask fitted with a wide bent tube about 16 inches long. The substance quickly melted, and, after a little free phenol had passed over, a somewhat viscid yellowish-brown liquid distilled. The residue consisted of charcoal, tarry matter, and alumina. The distillate weighed 268 grams, and after redistillation to remove a small quantity of aluminium phenylate

which was carried over, there remained 252 grams. This was separated by fractionation into three portions:—

- a. 52 grams, from about 80—200°.
- b. 160 grams, from 200—280°.
- c. 34 grams, above 280°.

Fraction a.—The greater part of this portion distilled between 178° and 184°, a small quantity of a very mobile liquid of the odour of benzene passing over at about 80°. By repeated distillation of this higher boiling point product, and rejecting small portions above 180°, a considerable part of it was obtained boiling between 178° and 180°. This liquid was colourless; it was soluble in a solution of potash, crystallised on cooling in long needles; gave hydrogen with the aluminium-iodine reaction, and, on combustion with oxide of copper, yielded 76·57 per cent. of carbon and 6·79 of hydrogen. The principal part of this fraction consisted, therefore, of phenol.

Fraction b.—This portion was shaken repeatedly with three or four times its volume of boiling water to remove any phenyl alcohol not separated by distillation. The residual oily liquid was dried over calcium chloride, and subsequently distilled several times, each time rejecting whatever failed to pass over below 300°. The distillate was now quite colourless, and nearly the whole of it boiled constantly at 249°.

This substance was not miscible with water or aqueous potash, and did not yield hydrogen by the aluminium-iodine reaction. It separated from an alcoholic solution, on cooling to a low temperature, in colourless prisms. Its specific gravity was 1·0904.

Burnt with oxygen and copper oxide—

- I. 0·3658 gram gave 1·1320 gram CO₂ and 0·1955 H₂O;
- II. 0·4241 „ „ 1·3175 gram CO₂ and 0·2279 H₂O;

results which appear from the following comparison to agree with the formula C₁₂H₁₀O, which is that of *phenyl ether*, described by Hoffmeister in 1871 (*Ber.*, 3, 747).

			I.	II.
C ₁₂	144	84·70	84·40	84·72
H ₁₀	10	5·88	5·93	5·97
O	16	9·42	—	—
	<hr/>	<hr/>		
	170	100·00		

Its index of refraction for A was 1·5675 at 25°, and the length of the spectrum, from A to H, was 0·0583. Two determinations gave 90·05 and 90·22 as the refraction equivalent for A, which accords with theory.

Portions of this compound were found to solidify to a mass of colourless prismatic crystals, while other portions apparently identical remained liquid. A few experiments were made in the hope of elucidating this anomaly. A quantity of the freshly distilled compound was well shaken in a stoppered bottle. No solidification occurred. A crystal of the substance was now introduced, and immediately beautiful star-shaped crystals formed on several parts of the introduced crystal, others forming on these, and the whole liquid speedily passed to the crystalline condition. This change was accompanied by a rise in temperature of 8° . Another portion of the substance remained liquid at 2° for hours, but quickly solidified on the vessel containing it being immersed in a freezing mixture.

Fraction c.—This portion consisted of a viscid brown liquid, containing grains of a yellow solid. It was distilled a number of times, rejecting each time a small quantity of a non-volatile tarry substance. The distillate was now less viscid and much lighter in colour. On slowly distilling it, an almost colourless liquid passed over at about 280° , which condensed to a nearly white solid; and this was followed at a higher temperature by a comparatively small quantity of a non-crystallisable, thick orange-coloured liquid.

The solid was purified by repeated solution in, and crystallisation from, alcohol of sp. gr. 0.880. It was white in colour, soluble in absolute alcohol, and more so in ether. It melted at 97° , and sublimed slowly a little below this temperature.

On combustion with oxygen and copper oxide after drying at 100° :

I.	0.1275 gram	gave	0.4018 CO_2	and	0.0654 H_2O
II.	0.1268	„	0.3987	„	0.0646 H_2O
III.	0.1933	„	0.6099	„	0.1005 H_2O

The third portion (III) analysed had undergone sublimation. The results expressed in parts per 100 give—

	I.	II.	III.
C	85.94	85.75	86.03
H	5.70	5.66	5.77

On the determination of its vapour-density by the method of Victor Meyer—

0.0978 gram	gave vapour = in volume	12.04 c.c. (corr.)
0.0836	„	10.19 „

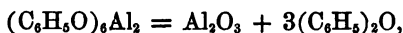
These data give 181.4 and 183.0 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $\text{C}_{12}\text{H}_{10}\text{O}$.

		Calc. for 100 pts.	Found (mean).
C ₁₃	156	85.71	85.91
H ₁₀	10	5.50	5.71
O	16	8.79	—
	<hr/> 182	<hr/> 100.00	

Three compounds of this formula have been described—fluorene alcohol, and diphenyl ketone, and its isomer. Our body does not accord in physical properties with the description of any one of these compounds. We are inclined, however, from the mode of its formation, to regard it as a phenyl ketone.

It would appear, then, from these results:—

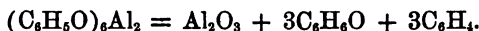
1st. That about half of the phenylate was resolved by heat into phenyl ether and alumina, thus—



which action gives a simple method of preparing this ether.

2nd. That a compound of the formula C₁₃H₁₀O was formed in relatively small quantity.

3rd. That about one-quarter of the aluminium compound was resolved very probably in accordance with the equation—



No evidence was found of the existence of the hydrocarbon C₆H₄, shown in this scheme, but it is not improbable that it existed in admixture in that portion of the distillate above 300°, which was richer in carbon than any of the bodies separated; in fact it contained 87.5 per cent., and its specific refraction and dispersion were very high.

Aluminium Para-cresylate.

760 grams of aluminium para-cresylate were heated as in the case of the phenylate. The distillate was almost solid when cold, yellowish-brown in colour, and weighed 463 grams. This product was boiled with 6 litres of alcohol, sp. gr. 0.805, and filtered from alumina by a calico strainer, supported in a hot water funnel. On cooling, a yellow crystalline substance separated, which, after washing with 9 litres of alcohol, weighed when dry 71 grams. This body was dissolved in alcohol, and crystallised therefrom, until the menstruum was free from yellow colour. After drying at 100°, the body was burnt with oxygen and copper oxide.

I. 0.1622 gram gave 0.5097 gram CO₂ and 0.0956 gram H₂O.

This substance was, however, still yellow, and when melted exhibited a blue fluorescence. It was slowly distilled, when nearly the

whole passed over at 307° . The distillate was of the colour of pale hock, free from the blue fluorescence, and solidified on cooling to a cream-coloured crystalline mass. This was dissolved in boiling alcohol, from which solution the substance separated on cooling in very thin plates, white in colour, and of a pearly lustre.

On combustion—

II. 0.1619 gram gave 0.5081 gram CO_2 , and 0.0989 H_2O .

The substance permitted of sublimation, and by the following method was obtained in long white lustrous plates. The compound in the condition of the white plates was melted and poured into a porcelain boat, and placed in the forepart of a glass tube about $1\frac{1}{2}$ inch in diameter, through which a current of hydrogen was passing. The part of the tube in proximity to the loaded boat was heated, and the boat and the flame slowly moved backwards as the compound sublimed.

On combustion—

III. 0.1205 gram gave 0.3774 gram CO_2 , and 0.0717 gram H_2O .

These results expressed in parts per 100 give—

	I.	II.	III.
C	85.70	85.59	85.70
H	6.54	6.78	6.52

On the determination of its vapour-density—

0.1186 gram gave vapour = in volume 12.64 c.c. (corr.)

0.1179 " " " 12.60 "

These determinations were made in hydrogen, and give 209.4 and 208.8 respectively for the molecular weight of the substance. The most probable molecular formula of the compound is therefore $\text{C}_{15}\text{H}_{14}\text{O}$.

		Calc. for 100 pts.	Found (mean).
C_{15}	180	85.71	85.66
H_{14}	14	6.66	6.61
O	16	7.63	—
	<hr/>	<hr/>	
	210	100.00	

It melted at 168° , and dissolved but slightly in alcohol, giving 2.5 per cent. at the boiling temperature, and 0.4 per cent. at 20° .

The alcoholic liquids obtained in the operations just described were distilled. About 10 grams of the solid compound separated, and after the alcohol had passed over, the residual liquid began boiling at 190° , gradually rising beyond the limits of the thermometer. The greater part however (120 grams) distilled between 190° and 300° . This

fraction was digested with successive portions of aqueous potash, and the alkaline liquid subsequently neutralised with hydrochloric acid. 36 grams of an oily brown liquid separated, which, after washing with a little water, and drying with calcium chloride, boiled for the most part between 199° and 202° . This distillate was colourless, and had the composition, refraction, and other physical and chemical qualities of para-cresol.

The portion of the fraction not soluble in aqueous potash was of a dark, yellowish-brown colour. It was washed with water, and digested with calcium chloride. It was now distilled about thirty times, each time rejecting small portions above 300° , and below points gradually rising from 220 — 270° . The distillate was colourless at this stage, and on cooling to a low temperature, formed a semi-fluid mass containing colourless prismatic crystals. This product was dissolved in about twice its volume of warm alcohol, from which solution, on cooling to a low temperature, the substance separated in prisms. It was dried at 100° , and burnt with copper oxide.

- I. 0.1070 gram gave 0.3324 CO_2 and 0.0710 H_2O .
 II. 0.0942 " " 0.2928 " " 0.0597 "
 III. 0.1541 " " 0.4793 " " 0.0972 "

These results expressed in parts per 100 give—

	I.	II.	III.
C.....	84.72	85.30	84.82
H.....	7.37	7.04	7.00

On the determination of its vapour-density—

0.1077 gram gave vapour = in volume 12.13 c.c. (corr.).
 0.1040 " " " " 11.75 "

These numbers give 198.1 and 197.6 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $\text{C}_{14}\text{H}_{14}\text{O}$ —

		Calculated.	Found (mean).
C_{14}	168	84.84	84.94
H_{14}	14	7.07	7.13
O	16	8.09	—
		<hr/> 100.00	

which would be that of cresyl ether, and from the general analogy between its properties and mode of preparation and that of phenyl ether, little doubt can exist as to the compound being the second ether of the phenyl series. As it was obtained through the aluminium derivative of para-cresylate, we name the compound *para-cresyl ether*.

This compound melts at $50^{\circ}\text{C}.$, is very soluble in ether and in benzol, moderately so in alcohol, and has an odour resembling that of phenyl ether, but fainter.

The action of heat on aluminium cresylate, as was to be expected, presents a general similarity to the action of the same agent on the analogous phenyl compound. The points of difference in the two cases are to be found in the variations in the amount of the corresponding compounds produced. The aluminium phenylate, for example, yields a relatively large quantity of phenyl ether, while the cresyl-aluminium alcohol gives only a relatively small quantity of the corresponding compound. Again, the phenyl compound yields only a small quantity of the $\text{C}_{18}\text{H}_{10}\text{O}$ body, while the cresyl compound yields a relatively large quantity of the homologue $\text{C}_{18}\text{H}_{14}\text{O}$. The hypothetical hydrocarbon C_7H_8 has not been found.

Aluminium Thymolate.

1000 grams of this compound were heated as in the cases of the analogous phenyl and cresyl compounds. A little free thymol at first passed over, then an orange viscid liquid, which partially solidified on cooling. As soon as the thymolate became fluid by heat, it was noticed to be in violent commotion, evidently from the passage through it of gas. The nature of this gas, and the meaning of its evolution, were determined.

45 grams of thymolate were heated until gas evolution practically ceased. The gas for the first 3240 c.c. was a pure olefine, after which it consisted of a mixture of the olefine and probably marsh-gas, the latter compound being evolved in an increasing ratio towards the completion of the action. The total gas collected (corr.) measured 5856 c.c., of which 5032 c.c. combined with bromine.

In another experiment, employing 230 grams of thymolate, 196 grams of an olefine bromide were obtained. The greater part of this compound boiled, on rectification, between 136° and 139° . Its sp. gr. at 4° was 1.913, and when dissolved in alcohol and treated with zinc it gave zinc bromide and a gas burning with very luminous flame. The gas set free on heating the fluid thymolate is therefore propylene.

The distillate from the 1000 grams of thymolate weighed 470 grams. It was divided by distillation into two portions:—*a*, which passed over below 280° , and *b*, above that temperature.

Fraction a.—This portion was liquid, of a brownish-yellow colour, and weighed 207 grams. It was treated with successive quantities of a warm solution of potash, in which it partially dissolved. The alkaline solutions obtained were neutralised with hydrochloric acid, when a

brownish oily liquid separated, which was dried over calcium chloride and distilled. The distillate was redistilled some five or six times, each time rejecting the portion not passing over below 205° . The distillate at this stage was colourless, and nearly the whole of it distilled between $196-202^{\circ}$.

On combustion with copper oxide and oxygen—

0.1820 gram gave 0.5164 gram CO_2 and 0.1208 gram H_2O .

The substance gave hydrogen with the aluminium reaction, and readily dissolved in aqueous potash. Its refractive index for A was 1.5316 at 23°C . These qualities, jointly with its composition exhibited in the following comparison, show the compound to be cresol:—

	Calculated.	Found.
C_7	77.77	77.38
H_8	7.40	7.37
O	14.83	15.25 (by diff.)
	<hr/> 100.00	

Moreover, as this substance did not solidify at a temperature of -17°C ., we concluded that it is meta-cresol. Hitherto this modification had not been seen in the solid condition, but on stirring the product just described with a thermometer, it underwent solidification at -14°C .

Fraction b.—This portion consisted apparently of a yellow crystalline body in admixture with a brownish viscid liquid. It weighed 231 grams. After the addition to it of the high boiling portion of fraction *a*, the product was mixed with about twice its volume of ether, and the mixture heated for a few minutes in hot water. On cooling in a freezing mixture the brown liquid remained in solution, while the solid was apparently unaffected. The solid was now washed on a filter with cooled ether. It quickly became white, and was then found to weigh 15 grams, and to consist of small shining scales. This body was next dissolved in boiling alcohol, sp. gr. 0.805, from which solution, on cooling, it separated in large white plates, having a pure pearly lustre. It was dried and burnt with copper oxide and oxygen with the following results:—

I. 0.1917 gram gave 0.6017 gram CO_2 and 0.1142 gram H_2O .

II. 0.2035 ,, 0.6383 ,, 0.1218 ,,

These data expressed in parts per 100 give—

	I.	II.
C.....	85.60	85.54
H	6.61	6.65

On the determination of its vapour-density—

0·1279 gram gave vapour = in volume to 13·66 c.c. (corr.).

0·1219 " " " 13·04 "

These numbers give 209 and 208·6 respectively for the molecular weight of the compound. Its molecular formula is therefore $C_{15}H_{14}O$ —

		Calc. for 100 pts.	Found (mean).
C_{15}	180	85·71	85·57
H_{14}	14	6·66	6·63
O	16	7·63	—
	<hr/> 210	<hr/> 100·00	

This compound permits of sublimation by the method used for the compound of the same molecular formula from para-cresol. It sublimes, however, much more readily, and forms larger crystals than that substance.

The ethereal liquids, obtained in the operation described, were distilled. The residuum, after the ether had separated, commenced distilling at about 250° , from which temperature to 300° an almost colourless liquid passed over. The portion above 300° , after distillation, was treated with about twice its volume of ether. On standing, more of the $C_{15}H_{14}O$ compound separated, and by distilling the ethereal solution itself, another quantity of liquid was obtained, boiling between 250° and 300° . These operations were performed on the residue boiling above 300° until no more of the solid compound separated.

All the liquid obtained between 250° and 300° was now treated with a hot solution of potash, then washed with water, dried over calcium chloride, and distilled. The liquid commenced boiling at about 270° . It was distilled some 40 times, each time rejecting small quantities boiling above 300° . The liquid had now a faint yellow tinge, and boiled for the most part between 284° and 288° C. Its index of refraction for α was 1·5576 at 16° C. Burnt with oxygen and copper oxide—

I. 0·1500 gram gave 0·4676 gram CO_2 and 0·0963 gram H_2O .

II. 0·1765 " 0·5488 " 0·1136 "

These results expressed in parts per 100 give—

	I.	II.
C	85·01	84·80
H	7·13	7·15

On the determination of its vapour-density—

0·0929 gram gave vapour = in volume to 10·68 c.c. (corr.).

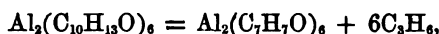
0·1176 " " " 13·56 "

These numbers give 194.16 and 193.58 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $C_{14}H_{14}O$ —

		Calc. for 100 pts.	Found (mean).
C_{14}	168	84.84	84.91
H_{14}	14	7.07	7.14
O	16	8.09	7.95 (by diff.)
	<hr/> 198	<hr/> 100.00	<hr/> 100.00

which is that of cresyl-ether. The physical properties of this substance, however, differ materially from those of the cresyl-ether discovered among the products of the aluminium para-cresylate. For example, it does not solidify even in a freezing mixture, or crystallise from alcohol. We are disposed therefore to regard it as isomeric with the ether of para-cresol, and from the mode of its formation to name it *meta-cresyl-ether*.

It appears then that heat readily resolves aluminium thymolate into aluminium meta-cresylate and propylene, thus—



and further, that the same agent splits up the aluminium compound so produced into alumina, meta-cresol, meta-cresyl-ether, and the pearly compound $C_{15}H_{14}O$, which, judging from the want of agreement between the physical properties of this substance and the one of the same molecular formula from the para-cresylate, would appear to be isomeric with this latter compound. The points of difference referred to are set out in the table below:—

	Melting point.	Solubility in abs. alcohol		Solubility in benzol 21° C.
		Boiling.	20° C.	
$C_{15}H_{14}O$ from para-cresylate	168°	2.5 p. c.	0.4 p. c.	3.3 p. c.
$C_{15}H_{14}O$ from meta-cresylate (thymolate)	200	1.0 „	0.17 „	0.93 „

Both of these substances are alike in one special particular, that of giving out a bluish-white light when shaken or rubbed.

Two substances of the formula $C_{15}H_{14}O$ have already been described, viz., para-ditolyl and di-benzyl ketones. Our compounds do not accord in physical properties with either of these bodies. From the composition and mode of formation we are, however, inclined to regard them as ketones, and provisionally as para- and meta-cresyl ketones respectively.

Aluminium β -Naphthylate.

150 grams of β -naphthol were heated with 10 grams of aluminium until the evolution of hydrogen nearly ceased. Some of the metal remained in the free condition, which is doubtless to be attributed to the infusible character of the resulting naphthylate preventing the completion of the action.

On distilling the mixture of naphthol and naphthylate a reddish-brown viscous liquid was obtained, which solidified on cooling. It was divided by distillation into two portions:—*a*, which passed over below 300° , and *b*, above this temperature.

Fraction a weighed 40 grams, and consisted of naphthalene and naphthol in about equal proportions.

Fraction b.—This portion was solid and dark yellowish-brown in colour. It was dissolved in boiling alcohol, and the yellow crystalline substance, which separated as the solution cooled, again and again crystallised from the same liquid. This product was next dried and twice distilled, which it did at a temperature above the limits of the thermometer. On cooling, the distillate formed a crystalline mass pale yellow in colour. It was crystallised from boiling alcohol until the menstruum was free from colour. The substance now separated from alcohol in thin pearly white rhomboidal plates. It melted at 104° C., and on combustion—

I. 0.2713 gram gave 0.8837 CO_2 and 0.1268 gram H_2O .

II. 0.2874 " 0.9359 " 0.1354 "

These results expressed in parts per 100 give—

	I.	II.
C	88.83	88.81
H	5.19	5.23

On the determination of its vapour-density—

0.1219 gram gave vapour = in volume 10.16 c.c.

0.1341 " " " 11.02 "

0.1399 " " " 11.64 "

These numbers give 267.8, 271.4, and 268.7 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $\text{C}_{20}\text{H}_{14}\text{O}$ —

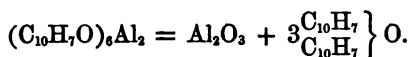
		Calculated.	Found (mean).
C_{20}	240	88.84	88.82
H_{14}	14	5.18	5.21
O	16	5.98	5.97 (by diff.)
	<hr/> 270	<hr/> 100.0	

which would be that of a naphthyl ether. As the body was formed by the decomposition of the β -naphthylate we name it provisionally *β -naphthyl ether*.

The alcoholic liquids obtained in the operations just described were distilled. After the alcohol had passed over the residuum commenced boiling at 290° , but quickly rose beyond the limits of the thermometer. A dark-brown viscous liquid distilled. This dissolved readily in alcohol, and the resulting solution very slowly deposited a quantity of the solid body just described. When this body had ceased separating a comparatively small quantity of a very viscous substance was obtained on distillation, containing 89.5 per cent. carbon and 5.3 per cent. hydrogen. It freely dissolved in alcohol, the solution exhibiting a blue fluorescence.

On distilling the several highest boiling point portions collected in the above operations a semi-solid distillate was obtained, which on treatment with boiling alcohol left a dark-yellow crystalline substance. This separated from benzene in square dark golden-yellow shining plates. It dissolved very slightly in alcohol, to which a mere trace imparted a powerful blue fluorescence. The quantity obtained was too small to determine its molecular formula, but a combustion showed it to be a very highly carbonaceous hydrocarbon, probably contaminated with a small quantity of an oxygenated body. For future reference we propose, from its double colour, the temporary name of *chryseudiene*.

The principal product of the decomposition by heat of β -aluminium naphthylate is β -naphthyl ether, thus:—



Aluminium- α -Naphthylate.

In order for aluminium to replace the basic hydrogen in α -naphthol the usual quantity of iodine must be employed. This difference between the α - and β -modification serves to discriminate the two naphthols.

520 grams of α -naphthylate were prepared in the manner ordinarily used for the aluminium-derivatives of the other alcohols. This compound underwent decomposition on heating, but the temperature required was much higher than in the case of the analogous β -compound. A brownish-yellow viscous liquid distilled, which solidified on cooling, and weighed 319 grams. This product was separated by distillation into two portions: *a*, which passed over below 310° , and *b*, above this temperature.

Fraction a weighed 90 grams, and mainly consisted of naphthalene.

Fraction b.—This was melted and poured into about twice its volume of boiling alcohol. A quantity of a yellow substance remained undissolved, and a little more separated on the cooling of the alcoholic liquid. These operations were repeated four times on the yellow body successively obtained. The substance was now distilled, and on cooling the distillate solidified to a yellow crystalline mass. This was crystallised some four times from benzene, in which it dissolved more readily than in alcohol. It now separated in large shining rhombic plates of the colour of uranium glass. Burnt with copper oxide—

I. 0.2694 gram gave 0.9302 gram CO_2 and 0.1342 gram H_2O .

II. 0.2816 " 0.9741 " 0.1408 "

These results expressed in parts per 100 give—

	I.	II.
C	94.17	94.34
H	5.53	5.55

On the determination of its vapour-density—

0.1026 gram gave vapour = in volume to 9.06 c.c.

0.1029 " " " 9.06 "

These numbers give 253.0 and 253.4 respectively for the molecular weight of the substance. Its most probable molecular formula is therefore $\text{C}_{20}\text{H}_{14}$.

		Calculated.	Found (mean).
C_{20}	240	94.43	94.26
H_{14}	14	5.57	5.54
	<hr/> 254	<hr/> 100.00	<hr/> 99.80

Three compounds of this formula are known, viz., $\alpha\alpha$ -, $\alpha\beta$ -, $\beta\beta$ -dinaphthyls. The substance described resembles in physical properties the $\beta\beta$ -dinaphthyl of Mr. Watson Smith. It dissolves in hot oil of vitriol, forming a light green, and subsequently a blue colour, and melts at 189° .

The residue left after distilling off the benzene from the liquids obtained in the purification of the hydrocarbon just described was boiled with alcohol, in which the greater part dissolved. On cooling a substance separated, which, after many crystallisations, formed long flat buff-coloured needles. When burnt with copper oxide it gave, as the mean of two determinations, 90.8 per cent. carbon and 5 per cent. of hydrogen. And two determinations of its vapour-density gave for mean 132.6. It would appear from these results that the substance is not a single compound. We are inclined to regard it in fact as

consisting of a $C_{20}H_{14}O$ or $C_{21}H_{14}O$ body in admixture with dinaphthyl.

The alcoholic liquids from fraction *b* were distilled. After the alcohol had passed over a brown viscous substance distilled, containing 90.38 per cent. of carbon and 5.21 per cent. of hydrogen. It dissolved readily in alcohol, the solution exhibiting a blue fluorescence.

The action of heat on the two aluminium naphthylates is seen to be very different. The β -compound splits up at a lower temperature than does the α , and yields as the principal product naphthol-ether, while it is doubtful whether an ether is formed at all in the case of the α -compound.

Though these aluminium alcohols are more or less distillisable at reduced pressures, they are alike decomposed by heat at the ordinary pressure of the atmosphere. The products of the decomposition of the series $C_nH_{2n+1}OH$, $C_nH_{2n-7}OH$, and $C_nH_{2n-13}OH$, appear, however, to be somewhat different. The first series yields the corresponding ethers, alcohols, and olefines; the second, the corresponding ethers and alcohols (with the exception of the thymolate, which suffers reduction to cresylate in the first stage of the action), together with crystalline bodies hitherto undescribed, and probably consisting of ketones. The third series gives in one case the corresponding ether and probably alcohol, together with hydrocarbons of a class differing from the olefines.

IV.—On the Action of Oxides on Salts. Part IV.* Potassic Chlorate and Ferric Oxide.

By EDMUND J. MILLS, D.Sc., F.R.S., and GEORGE DONALD.

33. THE work accomplished in previous parts naturally led us to consider the decomposition of potassic chlorate by oxides, a reaction which, during the 50 years since Döbereiner† first observed it, has been, and still continues, a problem in theoretical chemistry.

There are several oxides which are known to facilitate the evolution

* For Part III see Journal, 1881, 1, 533.

† *Ann. Pharm.*, 1, 236. Döbereiner thus states the problem:—"Welche Rolle spielt nun der Braunstein in diesem Prozesse? wirkt er blos als guter Wärmeleiter oder als Electromotor? oder ist es endlich noch ein Minimum von inhärentem Wasser, welches die totale Zersetzung des Salzes bedingt und die Bildung des oxy-chlorsauren Kalis verhindert?"

of oxygen from potassic chlorate, and to prevent, perhaps entirely, the formation of perchlorate. Of these manganic dioxide is the most striking example. One of us, accordingly, in association with Mr. John Stevenson, M.A., made numerous experiments with this substance; but the investigation was eventually abandoned, partly because we were unable to prepare* a stable anhydrous dioxide, and partly on account of the irregularity and comparative violence of the reaction. We shall again refer to these results in a supplementary note.

34. The chlorate employed in our experiments consisted of a fair commercial sample, which was purified by repeated crystallisation and filtration. It was powdered, sifted, dried at 100°, and kept in dry air. The ferric oxide was prepared from a sample of pure ferrous sulphate by oxidation with hydric nitrate, precipitation by ammonia, complete washing, solution in hydric chloride, and reprecipitation with ammonia. Washing was again proceeded with, until the washings were free from chloride or sulphate. The hydrate was then dried over the water-bath and ignited, in successive small quantities, in a porcelain crucible. In order to preclude the gas flame which surrounded the crucible from attacking the oxide, the crucible was cemented into a circular aperture, cut centrally in a plate of iron about 2 feet square. All the ignitions were, as far as possible, carefully executed in the same manner. The residual preparations of oxide were all mixed together, powdered, and sifted through fine muslin. Renewed absorption of water was prevented by heating to 100°, and preservation in a desiccator.

35. The apparatus which was used for the reaction consisted of a shallow iron pot, inside which a low stage of porous tile was constructed; upon this stage lay the horse-shoe-shaped horizontal bulb of a Schlösing's regulator, and within the bulb was placed the porcelain crucible containing the mixture of oxide and chlorate. The crucible was covered with a lid, and the bulb of a mercurial thermometer was placed very near to it. The iron cover of the pot protected the whole arrangement. As a source of heat, we employed a Fletcher's burner, and the entire apparatus was, as far as could conveniently be managed, screened on all sides from draught.

36. The actual course of an experiment will suggest itself to the reader. All we need remark is (1) that the air-bath was heated for half-an-hour before each operation; (2) that the insertion of the crucible was an almost momentary act. Thus the time consumed in heating up the mixture of chlorate and oxide must have been very short; and the disturbance introduced into our work by this condition—especially when it is remembered that the duration of heating was always four hours—we regard as inappreciable. At the end of our

* Comp. Pickering, *Chem. News*, 43, 226.

experiment, the crucible was instantly removed, placed in a desiccator, and weighed the next morning.

37. Our trial series of experiments was performed with pure substances prepared by Mr. Pratt (Part II), in 1878. The constant weight of potassic chlorate was 5 grams; the weight of oxide ranged from 0.5 to 3.0 grams, and the mean temperature* was 189.8°. Under these conditions, the loss of oxygen amounted to 0.0083 gram to 0.0311 gram. We found, however, on repeating some of our work, that we could not obtain constant results, neither were these of sufficient magnitude to serve as a basis for accurate determinations of a "factor of chemical effect." This factor had values extending from 0.11200 to 0.35742, and amounted on the average to 0.20750. It was evidently necessary to obtain a larger evolution of oxygen. We therefore (now taking substances of our own preparation, and the same constant weight of chlorate) raised the temperature to about 195°.

38. In the course of our calculations, we have had occasion to use the following numbers, viz.:— $\text{KClO}_3 = 122.47$, $\text{Fe}_2\text{O}_3 = 159.92$, $\text{O} = 15.96$. Actual weights, appropriately divided by these figures, may be considered as expressed in "chemical units."

The temperatures reported below are very good means of quarter-hourly observations.

If the action of ferric oxide upon potassic chlorate be similar to that of an ordinary oxide on an ordinary salt, the numerical results should admit of representation under some form of the general equation—

$$E = \frac{\alpha xy}{x_r + y_r}.$$

In this, E is the chemical effect on oxygen expelled, x and y are respectively the masses of oxide and chlorate; x_r , y_r , are the residues of these masses after action; and α is a "factor of chemical effect," depending upon the particular conditions of chemical change.

In our calculations we have taken $x = x_r$, since the oxide remains constant in each experiment; and chemical units have been employed throughout. The necessary details will be found in the following Table:—

* All our temperatures are corrected for zero error and exposure. For the exposure correction the ordinary formula and the factor 0.00013 were employed.

TABLE XI.

Experiment.	Oxide taken.	α .	Oxygen expelled.	E.	α .	Temp. C.
	grams.		gram.			
I	0.10	0.00062532	0.0213	0.0013346	2.1437	195.6°
II	0.15	0.00093797	0.0312	0.0019559	2.0998	195.1
III	0.20	0.0012506	0.0230	0.0014411	1.1769	195.1
IV	0.25	0.0015632	0.0233	0.0014599	0.95862	194.7
V	0.50	0.0031266	0.0435	0.0027250	0.91900	194.7
VI	0.75	0.0046898	0.0591	0.0037230	0.85643	195.6
VII	1.00	0.0062532	0.0629	0.0039411	0.70656	194.9
VIII	2.00	0.0125064	0.0993	0.0062218	0.62468	194.7
IX	3.00	0.0187596	0.1246	0.0078070	0.58086	194.7
X	5.00	0.0312660	0.1563	0.0097932	0.52806	194.7
XI	8.00	0.050026	0.1900	0.011915	0.50688	195.1
XII	8.00	"	0.1103	0.0069110	0.29964	195.2
XIII	8.00	"	0.1158	0.0072556	0.31416	194.7
XIV	10.00	0.062532	0.1320	0.0082707	0.32591	195.1
XV	10.00	"	0.1228	0.0076942	0.30377	194.7

39. It is evident from the above results that the chemical effect of the oxide increases rapidly at first, and afterwards at a diminishing rate; and the numbers suggest that the values of α are inversely proportional to the values of x . In order to test this hypothesis, we took all the values of α excepting IX and X (the mean of the values at 8 grams* and 10 grams oxide respectively being assumed, instead of the single quantities there), and calculated the following equation:—

$$(\alpha - 0.27420)(x + 0.00095942) = 0.0029056.$$

A comparison between theory and experiment is given in the Table below:—

TABLE XII.

Experiment.	α calculated.	α found.
I	2.10770	2.14370
II	1.80560	2.09980
III	1.58890	1.17690
IV	1.42600	0.95862
V	0.98532	0.91900
VI	0.78854	0.85643
VII	0.67706	0.70656
VIII	0.48998	0.62468
IX	0.42155	0.58086
X	0.364367	0.52806
XI—XIII	0.331191	0.37356
XIV, XV	0.319965	0.31484

* In Experiment X it is probable that the temperature accidentally rose when the thermometer was not under observation, but as we are not certain of this explanation we have retained the result.

Probable error of a single comparison, 0.15215; of 12 comparisons, .043921. Sum of the errors, 0.023163. The hypothesis, therefore, with regard to α may be accepted as fairly correct.

40. Some of the relations between the acting quantities are worthy of special consideration. The factor α of chemical effect is the number of chemical units of oxygen expelled per unit of oxide.

Now since—

$$\alpha = \frac{0.0029056}{x + 0.00095942} + 0.27420,$$

it follows that when x is very small $\alpha = 3.3028$. Hence, within the limits of experimental error, Fe_2O_3 expels $\text{O}_{3.3}$, or $3\text{Fe}_2\text{O}_3$ expels O_{10} , when the weight of oxide is very small; and a unit of the oxide then acts on rather more than a unit of the chlorate. On the other hand, when x is very large

$$\alpha = 0.27240. \quad \text{Hence}$$

$$E = \frac{0.27240xy}{x + y},$$

an expression which, on the understanding stated, reduces to—

$$\begin{aligned} E &= 0.27240 y = 27240 \times 0.040826 \\ &= 0.01112 \text{ unit} \\ &= 0.1775 \text{ gram.} \end{aligned}$$

Assuming, then, the quantity of oxide to be indefinitely great, the 5 grams of chlorate would not, under the conditions of our experiments, have lost more than 0.1775 gram oxygen. This amount has not in fact been exceeded, except in Experiment IX, which we believe to be of an accidental character.

Another inference which may be drawn from our work is very obvious. As the mass of oxide increases, so does its efficiency decrease; it stands, so to speak, in its own way. Large quantities of oxide present little real advantage over medium quantities, such, for instance, as an equal weight.

There can be no doubt, if we compare our first with our second series of experiments, that the value of α rises with the temperature. The constant λ seems to depend on the physical condition of the oxide.

41. In Part II (23) of these researches, it was shown that the action of ferric oxide on 5 grams potassic carbonate leads to the expulsion of carbonic dioxide in three stages, and that in the first of these (*i.e.*, from 2.4 grams oxide downwards) the factor of chemical effect is inversely proportional to the mass of the oxide. Thus the entire course of the action of ferric oxide upon potassic chlorate is strictly analogous to the first stage of the action of the same oxide on potassic

carbonate; and both actions are particular cases of the general effect of an oxide on a salt represented by the equation—

$$E = \frac{axy}{x_r + y_r}$$

It is obvious, then, that the case of chemical change which we have had under consideration presents nothing abnormal or peculiar in its features. From the carbonate, an oxide of carbon is the matter expelled; from the chlorate, an oxide of oxygen. The law of action is the same in both instances. The name *catalysis*, therefore, which was applied by Berzelius to this case of chemical change, ceases to have any reason for its existence.

SUPPLEMENTARY NOTE.

Manganic Dioxide and Potassic Chlorate.

By EDMUND J. MILLS, D.Sc., F.R.S., and JOHN STEVENSON, M.A.

42. As stated in (33) we performed a number of experiments with manganic dioxide. The particular mode of preparation which we eventually selected was that of Beilstein and Jawein (*Ber.*, 1879, p. 1528), which leads to a body really consisting of manganic dioxide in a hydrated condition. Our hydrate contained 3·31 per cent. of water. With this preparation we uniformly obtained a very violent action at 210°. As previous trials with this and another sample of hydrous dioxide had convinced us that evolution of oxygen begins at about 160°, we selected an intermediate temperature (180°), the time being four hours, and the weight of chlorate 5 grams. With quantities of oxide less than 0·05 gram we obtained only very irregular results; but with that quantity and higher weights, the values of α were fairly satisfactory.

[$\text{MnO}_2 = 86\cdot92$.]

TABLE XIII.

Anhydrous oxide.	α .	Oxygen expelled.	α found.	α calculated.
0·0483	1	0·4361	38·838	39·175
0·0967	2	0·6087	24·567	24·034
0·4835	10	0·7731	6·451	6·486
0·9669	20	0·7543	3·767	3·789
1·9338	40	0·7798	2·517	2·386
4·8345	100	0·7416	1·657	1·528
9·6690	200	0·6482	1·239	1·239

The above calculation has been simplified by taking proportional

values for x . The "anhydrous oxide" is calculated from a determination of water lost at 280—300°, and the "oxygen expelled" by deducting the loss of water by the hydrate at 180° from the total loss. The equation is—

$$(\alpha - 0.94800)(x + 0.52577) = 58.310.$$

Probable error of a single comparison of theory with experiment, 0.18123; of seven comparisons, 0.068499.

43. The relation which we have indicated between α and x rests upon a certain supposition. The percentage of water present in the hydrate was 3.31 at the beginning, and 0.144 at the close of the reaction; and this amount might very possibly have been sufficient, in accordance with Döbereiner's suggestion, to furnish an incentive for the powerful effects in the 0.0483—9.6690 gram experiments. On the other hand, it might have produced no such effect, but may have had influence merely in retarding the evolution of oxygen in the <0.0483 gram experiments, as seems to have been the case. What we can say with considerable confidence is, that in either event, the effect upon the form of the relation α to x of the presence of this quantity of water in the oxide is not traceable; the action of manganic dioxide upon potassic chlorate resembles the ordinary behaviour of an oxide towards a salt.

V.— α - and β -Amylan: Constituents of some Cereals.

By C. O'SULLIVAN.

FROM amongst the constituents of a few cereals, I have succeeded in isolating two bodies which possess some points of interest in consequence of the relation they appear to hold to the starch group of carbohydrates. This interest is considerably increased when the position which the bodies, dextran (Scheibler, *Zeitschrift für Rübenzucker Industrie*, 1874, 309) and lævulan (Lippemann, *Ber.*, 14, 1509), seem to occupy to the cane-sugar group, is taken into consideration.

The method employed in the preparation of the bodies from barley, skinless barley, wheat, and rye, may be described as follows:—

The finely-ground grain was treated with alcohol (sp. gr. 90) at 40° as long as anything was dissolved. Certain albuminoids, sugars (cane-sugar, lævulose, and dextrose), &c., were thereby removed. The residue, pressed as free as possible from alcohol, was treated with a large bulk of water (10 or 12 times the weight of the cereal em-

ployed), and the temperature of the mixture maintained at 35° to 38° for several hours, with continual stirring. The insoluble portion was allowed to settle, the fairly clear supernatant liquid was decanted off, more water at 40° added, and the process repeated as long as anything was dissolved. It was difficult to obtain the solution absolutely clear, but a few filtrations through moderately good filtering cloth freed it from starch. The solution thus freed was submitted to evaporation, whereupon a white gummy skin began to form on the surface, the removal of which facilitated the process. As soon as the solution became fairly thick, the removed gummy matter was stirred into it and the liquid allowed to cool. Alcohol (sp. gr. 0.83—0.84°) was then added as long as a precipitate formed. This precipitate was fairly white and stringy; it soon settled to a tough woolly mass. It was washed several times with dilute (0.88), then with strong (0.82), and finally allowed to stand for a few hours under absolute alcohol. The alcohol was then drained off, the residue pressed, and placed over sulphuric acid in a desiccator. In a short time it dried to an almost white friable mass, becoming electric on being powdered in an agate mortar. This apparently dry body lost at 100° in dry air 13 to 15 per cent. of its weight, and was found to contain 14 to 15 per cent. of ash, consisting of phosphoric acid, potash, magnesia, and lime. The ash from the body yielded by skinless barley, gave the following percentage composition:—

P_2O_5	=	38.15
K_2O	=	34.26
MgO	=	15.91
CaO	=	10.02
Loss, &c.	=	1.66
<hr/>		
100.00		

The constituents of the ash of the bodies obtained from the other cereals were not estimated. These bodies are no doubt the so-called vegetable mucilage in a rather pure state.

The raw product was treated with cold water as long as anything was dissolved; of that from barley and skinless barley, a large portion remained insoluble in the form of a crumby mass. For the present we shall neglect the solution. The crumby insoluble portion was treated with cold dilute hydrochloric acid (5 per cent.) for some days, and afterwards washed free from the acid by repeated treatment with cold water. It was then dissolved in boiling water, in which it at first melted, and filtered from a little flocculent matter. This operation, by the way, is long and tedious in the extreme, unless the solution be dilute, and, even then, it is far from what could be called a rapid process. The filtrate was concentrated, and

alcohol (0.83) containing 3 or 4 per cent. hydrochloric acid added. The precipitate was white and fibrous; it was washed free from hydrochloric acid with alcohol (0.86), and, after being pressed, was placed under absolute alcohol for a few hours. Again pressed as free as possible from the liquid, and placed over sulphuric acid in a desiccator, it soon dried to a perfectly white easily friable mass, becoming strongly electric when powdered in an agate mortar.

In order further to purify this body, it was again treated with cold water and acid, washed free from acid, dissolved in hot water, precipitated with alcohol, and dried. A few repetitions of this treatment yielded a snow-white body, containing not more than 0.3 per cent. of ash.

The substance, as will be seen from the mode of preparation, is almost insoluble in cold water; it melts, or probably gelatinises, in hot water, and, if the solution contains anything like 2 grams of dry substance in 100 c.c., forms a clear jelly-like fluid. A solution containing 1 gram of dry substance (dried in dry air at 100° and afterwards at 120° in an air-bath) in 100 c.c. at 15.5°, gave a specific gravity = 1.00396, and in a 200 mm. tube (Soleil-Scheibler) an optical activity at 15.5°* = -1.3 divisions or thereabouts; this gives $[\alpha]_D = -25^\circ$ for the body. Numbers varying between -22° and -26° were obtained for various preparations, and, I should say, -24 ± 2 contains the truth; but, in consequence of the low solubility and low opticity, it is difficult to determine the factor with any degree of accuracy. The number, however, with the other characters, is sufficient to establish the identity of the body.

A portion of the substance was dissolved in hot water, and alcohol added until a precipitate began to form. This was allowed to settle, and the supernatant liquid decanted off. The precipitate was dried as described above. To the decanted liquid more strong alcohol was added, and a further precipitate obtained. This was also dried. When the original body was so far purified as to give an optical activity $[\alpha]_D = -24$, the first and second precipitates yielded also the same opticity. Hence, the body in this state was a simple substance, and could be submitted to analysis.

When dried, it yielded on combustion in oxygen—

(a.)	(b.)
C = 44.39 per cent.	44.22 per cent.
H = 6.26 ,,	6.35 ,,

The formula $C_6H_{10}O_5$ requires—

C = 44.44 per cent.
H = 6.17 ,,

* All the optical observations mentioned in this paper were made at 15.5°—16°.

The body (a) was prepared from skinless barley and (b) from ordinary barley. I must not omit to state that oxygen had to be used to burn these bodies, as well as those hereinafter to be described, because I found that with cupric oxide alone, the carbon came out 1 to 1.5, and sometimes 2 per cent. too low, although the hydrogen seldom exceeded 6.35 per cent.

The substance is, therefore, a carbohydrate of the same percentage composition as starch. It does not reduce alkaline copper solution. Treated with a 5 per cent. sulphuric acid, and boiled for a short time, it is converted into dextrose; but if a 2 per cent. acid be employed, the time required for conversion is considerably increased, yet, even then, it is very much less than that required to convert starch or any of its transformation products into dextrose. It was, nevertheless, desirable to determine whether any of the bodies between starch and dextrose were produced in the process of conversion. For this purpose the strength of the acid was so regulated, that at the end of 30 minutes, the acid being separated with pure baryta-water, and the filtered solution evaporated until it contained 4 grams substance in 100 c.c., the body in solution was found to have the following characters:—

$$\begin{aligned} K \text{ (cupric oxide reducing power)} &= 88.3 \\ [\alpha]_j \dots\dots\dots &= + 46.72^\circ. \end{aligned}$$

The opticity of a mixture containing 88.3 per cent. of dextrose and 11.7 of the unaltered body is—

$$[\alpha]_j = + 47.41^\circ.$$

A portion of the solution in which the acid was not neutralised was digested for 15 minutes longer, and in a part of it the acid separated as before. The solid matter then in solution yielded the factors—

$$\begin{aligned} K &= 94.1 \\ [\alpha]_j &= + 51.6^\circ. \end{aligned}$$

A mixture containing 94.1 per cent. dextrose and 5.9 of the unchanged body yields an optical activity—

$$[\alpha]_j = + 52.2^\circ.$$

The portion of the solution which was not neutralised was digested for 15 minutes longer; the solid matter was then found to have the following properties:—

$$\begin{aligned} K &= 98.5 \\ [\alpha]_j &= + 56.2^\circ. \end{aligned}$$

The solution at this stage, freed from acid, was evaporated to a syrup, which on standing a few days yielded a crop of warty crystals; when the syrup was too concentrated, it solidified on standing. The

crystals yielded the leading factors of ordinary dextrose. Carefully dried at 100° in dry air, the temperature being gradually arrived at, they gave—

$$\begin{aligned} K &= 100 \text{ to } 102.5 \\ [\alpha]_D &= + 57^{\circ} \text{ to } 58^{\circ}. \end{aligned}$$

The body is, therefore, converted directly into dextrose without yielding any of the intermediate products furnished by starch. Although lævo-rotatory, and possessing many properties in common with Lippmann's lævulan, it is altogether distinct from that substance (lævulan yields lævulose when acted upon with sulphuric acid, and has an opticity $[\alpha]_D = -221$), and, inasmuch as it yields, like starch and the transformation products thereof (the amylan group), dextrose by the action of dilute sulphuric acid, I propose to call it *amylan*; and, in consequence of what I have to describe below, it would be best to designate it as α -*amylan*. When the body is dried without previous treatment with absolute or very strong alcohol, it is a white semi-transparent horny mass, resisting all efforts to pulverise it.

I have now to turn to the cold water solution, neglected in the preparation of α -*amylan* from barley and skinless barley. It was evaporated to a small bulk and allowed to cool. An excess of hydrochloric acid was added, and the mixture well shaken. The addition of alcohol (84°) yielded a bulky precipitate, the alcohol being added as long as anything fell out. This precipitate was washed with alcohol containing hydrochloric acid, and afterwards with pure alcohol, until the washings ceased to give a cloud with silver nitrate. It was then dried in the usual way, by treating with absolute alcohol, pressing that liquid out, and placing the pressed mass over sulphuric acid. On submitting the dried body to the action of cold water, only a small portion remained insoluble; the great bulk gelatinised and dissolved. The insoluble portion was found, from opticity, &c., to be α -*amylan*. The solution was evaporated until a trial portion became a jelly on cooling; the whole was then gradually mixed with alcohol, care being taken that as much of the substance as possible was retained in the form of a *milk* by the alcohol. I use the term "*milk*," because I can find no other word to express the appearance; the alcohol becomes a white opalescent liquid with very minute suspended particles which do not fall out on standing. If the aqueous solution were free from α -*amylan*, nearly the whole of the substance would be retained by the alcohol in this milky form. The addition of a few drops of hydrochloric acid with a little stirring, produced a white bulky flocculent precipitate. This soon settled and was washed and dried by treatment with alcohol, as described in the case of α -*amylan*. A few resolutions and reprecipitations in this way yielded a body free, or nearly so, from ash. Dried in dry air at 100° , and afterwards in

an air-bath at 120° , the substance thus purified gave the following factors. A solution containing 1 gram in 100 c.c. at 15.5° had a sp. gr. = 1.00392 to 1.00396, and an optical activity calculated on the dry body $[\alpha]_j = -72$ to -74 . Submitted to combustion it yielded—

$$C = 44.35 \text{ per cent.}$$

$$H = 6.28 \quad ,,$$

the percentage composition of starch.

Digested with dilute sulphuric acid it gave a little more than its own weight of a sugar having the same opticity and K, viz. :—

$$[\alpha]_j = + 55.5^{\circ} \text{ to } + 57^{\circ}$$

$$K = 100.5 \text{ to } 101$$

as ordinary dextrose. This solution, when concentrated to a syrup, did not, however, yield crystals on long standing.

In order to determine whether it was a simple body or a mixture, I proceeded in the same way as I had done in the case of α -amylan. It melts (gelatinises) readily and dissolves in cold water, a solution containing more than 1 gram in 100 c.c. being a quite thick fluid. I divided a portion into two parts by mixing with alcohol and partial precipitation, and found, upon the first attempt at separation, that the portion first precipitated gave, upon examination, a much increased optical activity; but, the second precipitate retained the original opticity. This result was rather puzzling. I felt at first inclined to think that I had at least two bodies to deal with. Further attempts at separation yielded a body gradually increasing in optical activity, until I obtained a product yielding,

$$[\alpha]_j = - 144 \text{ to } 148^{\circ}.$$

This I could not further increase, but I was able to separate it into two parts, each of which had the same opticity. The body worked with in this case was obtained from barley. Skinless barley yielded the same results. It seemed then probable that this soluble portion consisted of two bodies, one having optical activity $[\alpha]_j = - 144$ to $- 148^{\circ}$, and another much less; but as the opticity of the original body was $[\alpha]_j = - 72^{\circ}$, and as I could not obtain a less active substance from it, it was fairly obvious that the process of purification was effecting some change in the material. While these separations were being performed, I had a preparation of the same character in my hands, obtained from rye. The raw product from this cereal, that is, the precipitate from the aqueous solution, everything soluble in alcohol sp. gr. 90 having been previously removed, was found to contain but very little, not more than 3 or 4 per cent., of the insoluble (in cold water) crumbly body, α -amylan, the remaining 96 to 97 per cent.

being soluble after at first gelatinising. It was difficult to obtain portions of this substance capable of yielding solutions sufficiently bright for optical observation, yet at the earliest stages of the attempts to purify, specimens were obtained, the opticity of which I was able to satisfy myself, was below $[\alpha]_D = -80^\circ$. These bodies yielded more than their own weight of sugar, the K of which was 98 to 100° , and the $[\alpha]_D = +57$ to 58° (determined in solutions containing from 5 to 6 grams in 100 c.c.), and, therefore, so far agreeing with the factors of ordinary dextrose. In order, if possible, to remove the cause of the opalescence of solutions of the body, I boiled some of them for a time with lime, filtered, evaporated the bright filtrate to a thick liquid, allowed to cool, added excess of hydrochloric acid, and precipitated with alcohol. The precipitate was washed free from hydrochloric acid with alcohol, dried with absolute alcohol, pressed, and placed over sulphuric acid. The body thus prepared is almost exactly the same in general appearance as α -amylan, but on being submitted to the action of cold water it gelatinises to a transparent gum, and gradually dissolves, yielding a thick fluid solution which, when it contains little more than 1 gram in 100 c.c., flows very slowly.

The aqueous solution, containing 1 gram substance (dried in dry air at 100°) in 100 c.c. at 15.5° , was found to have a sp. gr. = 1.00394 to 1.00396. Determinations of the optical activity of the body in solutions containing from 0.6 to 1.3 grams in 100 c.c., gave numbers varying between $[\alpha]_D = -144^\circ$ and -148° . I may state that the low solubility, together with the short length of tube—200 mm.—at my disposal, did not admit of highly accurate observations; they were, however, sufficiently accurate for the purpose.

When the body so purified was divided into two or three portions by partial precipitation, each fraction was found to retain the opticity of the original body. It could, therefore, be looked upon as a simple substance. Dried in dry air at 100° , and afterwards at 120° in an air-bath, it gave on combustion—

$$C = 44.49 \text{ per cent.}$$

$$H = 6.24 \quad ,,$$

These numbers agree closely with those required by the formula $C_6H_{10}O_5$. Digested in a water-bath at 100° with a 5 per cent. solution of sulphuric acid for 30 to 35 minutes, the acid being separated with pure baryta-water, it yielded more than its own weight of solid matter having the

$$K = 100.9$$

$$\text{and } [\alpha]_D = 57.5^\circ;$$

the factors of ordinary dextrose. The solution evaporated to a syrup,

did not, however, even after standing six months, yield sufficient crystals for examination.

The substance is, therefore, the same as that described above as having been obtained from barley and skinless barley. Treatment with lime obviously converted it into a bi-rotatory modification. It was sufficiently easy to put this to the test with the barley body. A weighed portion of that body ($[\alpha]_D = -72^\circ$) was dissolved in water, and boiled with lime for a few hours. The solution, after filtration, was evaporated to a thick fluid, excess of hydrochloric acid added, and then alcohol as long as a precipitate formed. The precipitate when dried was within two or three per cent. (a loss to be easily accounted for) of the amount of substance employed. The optical activity of this body was found to be $[\alpha]_D = -144^\circ$; exactly double that of the body taken. That no other change took place will be obvious from the following:—

Dried as usual it gave—

$$C = 44.45 \text{ per cent.}$$

$$H = 6.13 \quad ,,$$

All these bodies left a slight ash in the platinum boat, but so slight was it from the 0.3 to 0.4 gram taken, that it was not indicated on a balance turning to half a milligram.

On digestion with sulphuric acid it gave a body, the factors of which were found to be—

$$\text{i} \dots\dots\dots K = 101 \text{ and } [\alpha]_D = +57.6^\circ$$

$$\text{ii} \dots\dots\dots K = 100.5 \quad , \quad [\alpha]_D = +56.4^\circ$$

These solutions, too, when evaporated to a syrup, did not crystallise satisfactorily. I have not as yet determined whether intermediate bodies are formed, but I have satisfied myself that neither maltose nor dextrin are produced.

Wheat, treated after the manner described above, yielded the same body, but I did not succeed in isolating the body α -amylan with any degree of satisfaction. Dried as usual it gave on combustion—

$$C = 44.56 \text{ per cent.}$$

$$H = 6.21 \quad ,,$$

and an opticity gradually increasing to—

$$[\alpha]_D = -144^\circ \text{ (1.2 gram in 100 c.c.)}$$

Treated with sulphuric acid it gave a body with—

$$K = 99.33$$

$$[\alpha]_D = +54^\circ \text{ to } +55^\circ.$$

This solution, too, on being concentrated to a syrup, did not yield

sufficient crystals for examination on standing for some months. In fact, while the sugar from α -amylan crystallised immediately on its solutions being evaporated to a syrup, that from the soluble body, whether prepared from the mono- or bi-rotatory modification, showed, under the same conditions, little tendency to crystallise.

This substance, whether it be prepared from barley, rye, or wheat, is like α -amylan and starch, a $C_6H_{10}O_5$ body, but it differs from the former in being soluble in cold water, in having an opticity three times as great, in yielding a bi-rotatory modification, and in giving, by the action of sulphuric acid, a dextrose possessing the same cupric oxide reducing power and opticity as ordinary dextrose, but showing less tendency to crystallise. This body may be conveniently known as β -amylan.

α - and β -amylan are interesting, not only for the light they throw upon the constitution of the mucilage of barley, wheat, and rye, but more particularly for the relation they appear to hold to the starch (amylum) group. When a mixture consisting of equal proportions of Scheibler's dextran and Lippmann's lævulan, bodies existing in beet in which cane-sugar is stored up, is submitted to the action of sulphuric acid, invert sugar is obtained, having the same opticity and K as that derived from cane-sugar. In the same way, a mixture containing α - and β -amylan (constituents of the cereals in which starch is stored up) in equal proportions, yields a product having the same opticity and K as that yielded by starch or maltose; hence the name *amylan* from the amyllum group.

Barley contains about 2 per cent. of α -amylan, and of β -amylan not more than 0.3 per cent.; indeed, the β -body is isolated with great difficulty from some barleys.

Wheat and rye contain from 2 to 2.5 per cent. of β -amylan, and the α -body is not present to a greater extent than 0.1 to 0.05 per cent.

In conclusion, I may state that I have not given all the analytical data, but I believe I have given sufficient for the purpose of the work, to characterise the bodies described.

Malted barley does not contain α -amylan; a body like β -amylan, but apparently much more soluble, can be isolated from it; of this I hope to have more to say on a future occasion.

VI.—*Note on the Action of Ethyl Chlorocarbonate on Benzene in presence of Aluminium Chloride.*

By EDWARD H. RENNIE, M.A. (Sydney), B.Sc. (London.)

It was shown some years ago by Wilm and Wischin (*Annalen*, 147, 150) that ethyl chlorocarbonate does not react with benzene, even when the two substances are heated together in sealed tubes, and that the former body decomposes, when heated to about 150°, into carbonic anhydride and monochlorethane. The idea suggested itself that possibly the two bodies might react at a low temperature in presence of aluminium chloride. On making the experiment, reaction commenced at once in the cold, large quantities of carbonic anhydride and hydrochloric acid being evolved, and *ethyl benzene* produced.

Subsequently it was found that ethyl chlorocarbonate, by mere contact with aluminium chloride in the cold, decomposes violently into carbonic anhydride and monochlorethane. The ethyl-benzene produced in the above reaction is therefore evidently due to the action of the liberated monochlorethane on the benzene.

When ethyl chloracetate is substituted for ethyl chlorocarbonate, no reaction takes place in the cold, and although some hydrochloric acid is evolved on heating, the desired result is not obtained, no ethylic phenylacetate being produced.

VII.—*On Benzyl-phenol and its Derivatives.*

By EDWARD H. RENNIE, M.A. (Sydney), B.Sc. (London.)

BENZYL-PHENOL was first prepared a few years ago by Paternò (*Gazzetta*, 2, 1), and further investigated by Paternò and Fileti (*ibid.*, 3, 121—251). These chemists state that by treatment with nitric acid, a nitro-compound may be obtained, and by treatment with bromine dissolved in carbon disulphide, a solid bromo-compound is produced; but these substances do not appear to have been very thoroughly examined. By the action of excess of sulphuric acid for about an hour at 100°, they obtained an uncrystallisable disulphonic acid, which yielded only uncrystallisable salts.

The following experiments were undertaken with the view of obtaining, if possible, more definite information regarding the deriva-

tives of this body. The benzyl-phenol used in the operations to be described, was prepared by the method given by Paternò, viz., by the action of benzyl chloride on phenol in presence of zinc. It was found advantageous to cool the mixture, otherwise the reaction becomes very violent, some of the liquid being often projected from the mouth of the flask. The crude product obtained by distillation was well pressed and crystallised from alcohol, and then melted at 84° , the melting point given by Paternò.

When concentrated pure sulphuric acid, slightly in excess of the quantity required theoretically for the formation of a monosulphonic acid, is added to some benzyl-phenol, and the mixture warmed on the water-bath for a few minutes, the whole dissolves to a clear liquid, which on cooling and standing for a short time solidifies to a crystalline mass. On dissolving this in water, adding ammonia, shaking up with ether to remove any unattacked phenol (which is moderately soluble in water), and then concentrating, an ammonium salt crystallises out in fine needles as the liquid cools. After recrystallisation it yielded, on analysis, the following numbers:—

0.5536 gram of the air-dried salt lost at 100° 0.0336 gram = 6.07 p.c.

Theory for $C_7H_7.C_6H_5(OH)SO_3.NH_4 + H_2O = 6.02$ per cent.

0.2423 gram burnt with oxide of copper by Dumas' method, gave 10.409 c.c. of nitrogen at 0° and 760 mm., equal to 0.0130115 gram = 5.37 per cent. Theory = 5.00 per cent. If potassium carbonate be used instead of the ammonium salt, proceeding otherwise as above, a potassium salt separates in groups of feathery crystals. On analysis it proved to be anhydrous, and gave the following results:—

0.6203 gram gave 0.1813 gram $K_2SO_4 = 0.08127$ gram K = 13.10 p.c.

Theory for $C_7H_7.C_6H_5(OH)SO_3K = 12.91$ per cent.

On adding barium chloride to a solution of either of the above salts, a barium salt separates out, which, after filtering off, may be dissolved in boiling water. On slow cooling it separates out in moss-like crystals. After drying in air they yielded, on analysis, the following results:—

0.501 gram lost at 100° 0.0132 gram = 2.63 per cent.

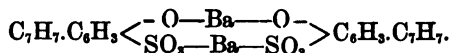
Theory for $[C_7H_7.C_6H_5(OH)SO_3]_2Ba + H_2O = 2.64$ per cent.

0.5454 gram gave 0.189 gram $BaSO_4 = 0.1107$ gram Ba = 20.41 p.c.

Theory 20.66 per cent.

If this barium salt be dissolved in hot water and barium hydrate, or barium chloride and ammonia be added, an almost insoluble basic salt separates in minute glistening crystals. A single analysis gave

36.5 per cent. of barium instead of 34.4 per cent. required for a basic salt of the composition—



The great difficulty of preventing the formation of barium carbonate in preparing this salt, will easily account for the high percentage of barium obtained on analysis.

All the salts of the acid, which have been examined, are but sparingly soluble in water, the mono-barium salt being much less soluble than the alkaline salts, and the di-barium salt almost insoluble. In order to isolate the acid, some of the pure potassium salt was dissolved in water, and acetate of lead added. A very insoluble lead salt was thereby precipitated, which was well washed, suspended in pure water, and decomposed by sulphuretted hydrogen. The clear filtrate was evaporated to a small bulk in a platinum dish, and then placed over sulphuric acid. In a few hours it solidified to a crystalline mass. The quantity hitherto obtained, however, is insufficient for a detailed examination. A further description will follow in a subsequent paper.

The acid and its salts give a splendid violet coloration with ferric chloride.

Potassium Nitro-benzyl-phenol-sulphonate.

If potassium benzyl-phenol-sulphonate be added in fine powder to dilute nitric acid (equal volumes of ordinary concentrated acid and water), keeping the liquid constantly stirred, a sparingly soluble crystalline yellow salt separates out. After recrystallisation and drying at 100°, it gave on analysis the following numbers:—

0.283 gram gave 0.0704 gram $\text{K}_2\text{SO}_4 = 0.03156$ gram $\text{K} = 11.15$ p.c.
Theory for $\text{C}_7\text{H}_7.\text{C}_6\text{H}_5.(\text{OH})(\text{NO}_2)\text{SO}_3\text{K} = 11.24$ per cent.

0.224 gram by Dumas' method gave 7.36 c.c. of nitrogen at 0° and 760 mm. = 0.0092 gram = 4.10 per cent.
Theory 4.03 per cent.

This salt is therefore a mononitro-benzyl-phenol-sulphonate. On boiling with potassium carbonate it yields an orange-coloured dipotassium salt.

Potassium Bromo-benzyl-phenol-sulphonate.

When one molecular proportion of bromine is added drop by drop to a solution of potassium benzyl-phenol-sulphonate, keeping the liquid in constant agitation, a white salt separates out, which on recrystal-

lisation from hot water separates in beautiful glistening scales. On analysing the anhydrous salt the following numbers were obtained:—

0.224 gram gave 0.05 gram K_2SO_4 = 0.0224 gram K = 10.00 p.c.

Theory for $C_7H_7.C_6H_5.(OH)Br.SO_3K$ = 10.23 per cent.

0.2108 gram gave 0.1036 gram AgBr = 0.44085 gram Br = 20.91 p.c.

Theory 20.99 per cent.

The salt is therefore a monobromo-benzyl-phenol-sulphonate.

Trinitrobenzyl-phenol.

If potassium or ammonium benzyl-phenyl-sulphonate in fine powder be added with constant agitation to an excess of ordinary concentrated nitric acid the salt dissolves easily, with scarcely any evolution of red fumes, forming a deep red liquid. If this liquid be exposed to the air in a shallow dish for several hours it becomes semi-solid from separation of a yellow crystalline substance. On diluting more of the yellow substance is precipitated. When well washed with water and recrystallised two or three times from boiling alcohol, the body separates in fine silky needles of a pale yellow colour. It is very sparingly soluble in cold alcohol, and only moderately soluble in the boiling liquid. A specimen crystallised three times melted at 148° , and after a fourth crystallisation the melting point was the same.

The following are the results of analysis:—

0.052 burnt in a vacuum with copper oxide gave 0.0067088 gram nitrogen, 12.90 per cent. N.

(The details of a combustion have been lost, the results only by some oversight having been entered in the note-book.)

	Found.		Theory for $C_{13}H_8(NO_2)_3OH$.
	I.	II.	
C	48.86	—	48.90
H	3.73	—	2.82
N	—	12.90	13.16

These numbers point clearly to a *tri-nitro*-derivative. The percentage of hydrogen is very high, but this was found to be due to the condensation of nitrous fumes in the drying tube. It was found extremely difficult to prevent their formation.

In order to confirm the above numbers some of the substance was boiled up with a dilute solution of pure potassic carbonate. It dissolved to a deep red liquid, which on cooling deposited small orange-

red needles of the potassium-derivative. The dry substance explodes when heated. On analysis it yielded the following numbers:—

- I. 0.069 gram gave 0.0164 gram K_2SO_4 = 0.00735 gram K.
 II. 0.1066 „ 0.0258 „ K_2SO_4 = 0.011565 „

These correspond to the following percentages:—

I.	II.	Required for dinitro-derivative.	Required for tri-derivative.
10.65	10.85	12.50	10.92

Constitution of the foregoing Bodies.

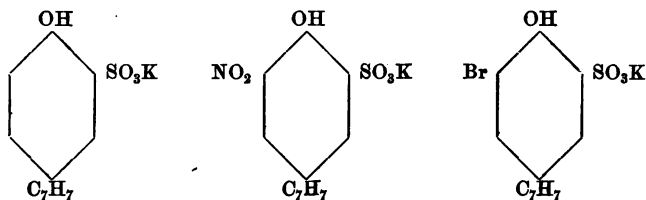
From the mode of formation of benzyl-phenol, from its properties, and from what is known of laws of substitution in phenol, there can be little doubt that it is a para-derivative. No direct proof of this has, however, been given. With the view of solving, if possible, this question, the methyl ether was prepared by digesting the phenol with the theoretical quantity of potassium hydrate, and a slight excess of methyl iodide mixed with some methyl alcohol in a flask attached to a reversed condenser. The action was complete in an hour or two. On distilling the product after thorough washing, the greater part came over from 305—315°. On redistilling this product, the greater part came over between 304° and 308°. The boiling point of this substance, as given by Paternò, who prepared it by the action of benzyl chloride on anisol in presence of zinc, is about 305°, and the product obtained as above agrees in all particulars with that previously described. On oxidation with chromic liquor, the ether yielded only benzoic acid (melting at 121°), but no anisic acid. This result evidently throws no light on its constitution. On oxidation with alkaline potassic permanganate, neither benzoic nor anisic acid is obtained, but a white crystalline substance easily soluble in alcohol and ether, and crystallising from the latter in fine prisms. This body is probably formed by the oxidation of the methylene (CH_2) group, and is in all likelihood a ketone, having the formula $C_6H_5.CO.C_6H_4.O.CH_3$. It is undergoing further investigation.

Oxidation with fused potash remains to be tried, but for want of material I have been compelled to leave it for the present. Should it fail to yield anisic acid, I hope to establish the constitution of benzyl-phenol by another method.

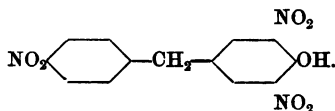
The great resemblance which benzyl-phenol shows to paracresol on treatment first with sulphuric acid and then with nitric acid and bromine, affords strong evidence in favour of the view that it is really a para-derivative.

Armstrong and Field have shown that when paracresol is treated

with sulphuric acid, an ortho-sulphonic acid is produced, and that when the salts of this acid are treated with dilute nitric acid or bromine, the other ortho-position (with regard to the OH group) is taken by the nitro-group or the bromine. The following formulæ therefore represent in all probability the constitution of the potassium salts above described:—



When potassium paracresol-sulphonate is treated with concentrated nitric acid, a diorthonitroparacresol is formed, whereas the corresponding potassium benzyl-phenol-sulphonate yields a *trinitro*-derivative. This is easily explained when it is remembered how easily the benzyl-group is nitrated. This trinitro-body very probably has the constitution:—



Should this be so, it would probably yield paranitrobenzoic acid on oxidation.

Experiments to decide this point, if possible, are in progress, and I hope soon to be in a position to lay before the Society the results of a further investigation of the whole subject.

VIII.—On the Steeping of Barley.

By EDMUND J. MILLS, D.Sc., F.R.S., "Young" Professor of Technical Chemistry in Anderson's College, Glasgow, and J. PETTIGREW.

1. IN the course of the processes which have for their object the preparation of malt from barley, the grain has to undergo a more or less prolonged immersion in water. Various kinds of natural water, some of them of scarcely compatible character, are highly esteemed for the purpose of this steeping. We have not, however, been able to

find any published statements * of a detailed description as to the action of water upon barley; and it appeared to us desirable to make an experimental outline, at least, of this undoubtedly complicated phenomenon. Our results are contained in the following paragraphs.

2. The barley we employed throughout our investigations was a fine sample of "chevalier," grown on limestone soil. Its analysis furnished the percentages recorded below—

Moisture.....	13.95
Nitrogen.....	1.87
Ash.....	2.23

3. The apparatus we employed consisted of a series of glazed cylindrical earthen pots, which were placed on a platform in a tank of water kept constantly running, and supplied from the main. Into each pot we introduced 300 grams of barley and 400 cc. of water, or some aqueous solution under trial, and the whole was covered with a glass plate. Each set of experiments, hereafter referred to in the tables, was made at one time, and under the same conditions. Temperatures were taken at noon by direct observation, and at midnight by an automatic recording thermometer; the mean of these temperatures is stated in each case.

4. It is obvious that, in working with a number of individual grains of barley, there may have been some whose outer coatings were injured, and which may have yielded extract with more than average rapidity; this is a source of error to which we are undoubtedly, though—as we believe, from actual inspection of many of the grains—but very little exposed. Moreover, to destroy other small errors, we always employed 300 grams of barley—a by no means inconsiderable weight; and for the sake of obtaining larger results, we prolonged the operation of steeping to 72 hours.

I. *Calcic Carbonate.*

5. A solution of calcic carbonate was made by passing purified carbonic dioxide through distilled water, in which well washed calcic carbonate was suspended. The filtered (saturated) solution contained .0896 per cent. of carbonate.

* Messrs. Lawes and Gilbert, in a Parliamentary Report (1866, Reprint, 1868) "On the Relative Values of Unmalted and Malted Barley," drew attention to the loss in steeping of "a certain amount of solid matter, which consisted of saccharine, nitrogenous, and mineral substances" (p. 22). They also found (p. 65) that the barley imparted 391.66 grains per gallon of solid matter (containing 8.62 grains of nitrogen) to the water they had occasion to employ. Our thanks are due to Dr. Gilbert for a copy of this Report.

Average temperature, 4·8° C.

TABLE I.

Experi- ment.	Carbonate in 100 c.c.	Residue from 100 c.c.	Ash from 100 c.c.	Extract in 100 c.c.	Nitrogen from 150 c.c.
I	0·0896	0·4817	0·3017	0·1800	0·00546
II	0·0672	0·4670	0·2870	0·1800	0·00742
III	0·0448	0·4582	0·2830	0·1752	0·00770
IV	0·0224	0·4440	0·2752	0·1688	0·00973
V	0·0000*	0·4015	0·2540	0·1475	0·00952

According to these numbers, as we diminish the amount of carbonate in the water, so the extract decreases. The nitrogenous constituents of the extract simultaneously increase up to Expt. IV; but distilled water extracts distinctly less of them than the ·0224 solution of calcic carbonate.

II. *Calcic Sulphate.*

6. This salt was prepared by bringing well washed chalk in contact with very dilute sulphuric acid, stirring frequently during three weeks, and filtering the neutral liquid.

Average temperature, 11·0°.

TABLE II.

Experi- ment.	Calcic sulphate in 100 c.c.	Residue from 100 c.c.	Ash from 100 c.c.	Extract in 100 c.c.	Nitrogen from 150 c.c.
I	0·2210	0·7240	0·4440	0·2800	0·00546
II	0·1657	0·7470	0·4296	0·3174	0·00616
III	0·1105	0·6000	0·3440	0·2560	0·00532
IV	0·0552	0·5480	0·3400	0·2080	0·00560
V	0·0000	0·5110	0·2760	0·2350	0·00716

Here also we notice that the extract decreases, *pari passu*, with the calcic sulphate from Expt. II to Expt. IV. The nitrogen and extract results are greatest of all at Expt. II. At Expt. V, as in the case of the carbonate, we get a disproportionate increase of nitrogen in the extract, but, in addition, a greater total extract. The total extract or nitrogen per unit of calcic salts is much greater with calcic sulphate than with carbonate.

* Distilled water alone was here used.

Burton Water.

7. Through the good offices of a friend, we were able to procure some water which is much used and held in great esteem for steeping purposes in Burton. The water is actually drawn at Lichfield, and our sample was turbid. In the following determinations we have compared it with a water analysed by the Rivers Commission (*Report*, p. 105), and described as being derived from a deep well in the new red sandstone at Lichfield. The numbers refer to parts per 100,000, excepting those relating to dissolved gases, which represent volumes per cent.

TABLE III.

		Rivers Commission.
Total solid matter.....	32·440	32·060
Organic carbon	—	0·163
Organic nitrogen	—	0·038
Ammonia	—	0·003
Nitric nitrogen	0·393	0·489
Silica	0·656	—
Magnesia (MgO)	1·412	—
Lime (CaO)	10·034	—
Sulphate (SO ₄).....	4·450	—
Chlorine.....	1·950	2·200
Hardness (temporary)..	7·070	9·300
„ (permanent) ..	11·100	9·000
„ (total)	18·700	18·300

Dissolved Gases.

Carbonic dioxide	3·0211	—
Nitrogen	3·4747	—
Oxygen	3·1080	—

The Rivers Commission considered their sample to have been polluted, as was doubtless the case with our own.

The measured effects of steeping are as follows:—

TABLE IV.

Experiment.	Residue from 100 c.c.	Ash from 100 c.c.	Extract from 100 c.c.	Nitrogen from 150 c.c.
I. Burton water	0·4540	0·2427	0·2118	0·00525
II. Half Burton water ..	0·4100	0·2207	0·1893	lost
III. Distilled water	0·4132	0·2230	0·1902	0·00630

Mean temperature 4·7°.

Here again the extract decreases as we approach to distilled water.

8. On account of the great importance of this particular water, we prepared two waters bearing a partial resemblance to it, and tried with them some steeping experiments. We shall call these liquids "Factitious Water A" and "Factitious Water B."

Factitious Water A.

Assuming the whole of the sulphate in the Burton product to be calcic, and all the chlorine to be sodic, we compounded this Water A, which was a solution of sulphate and chloride in distilled water, in the same proportions as we had found in the Burton supply.

Mean temperature, 6·9°.

TABLE V.

Experiment.	Residue from 100 c.c.	Ash from 100 c.c.	Extract from 100 c.c.	Nitrogen from 150 c.c.
I. Water A	0·4382	0·2430	0·1952	0·00448
II. Half water A	0·4734	0·2450	0·2284	0·00651
III. Distilled water	0·4132	0·2112	0·2020	0·00483

Thus, Water A gives rise on the whole to more extract and less nitrogen than the Burton sample. Water A and distilled water have about the same effect.

Factitious Water B.

9. Assuming the temporary hardness to be due to calcic carbonate, and the chlorine to be wholly sodic, we prepared this water so as to be a solution in these respects of the same composition as our Burton sample.

[The carbonate had been previously dissolved in carbonic water.]

Mean temperature 8·0°.

TABLE VI.

Experiment.	Residue from 100 c.c.	Ash from 100 c.c.	Extract from 100 c.c.	Nitrogen from 150 c.c.
I. Water B	0·4528	0·2872	0·2156	0·00488
II. Half water B	0·4630	0·2350	0·2280	0·00600
III. Distilled water	0·4334	0·2274	0·2060	0·00588

Like Water A, this water takes up most extract and most nitrogen at the half dilution, and in nearly the same absolute amount. Water B takes up less nitrogen than distilled water.

Supplementary Experiments.

10. We took occasion to examine several of the liquids in which we had steeped barley.

All the solutions and ashes contained phosphates. In the gypsum solution there was an alkaline sulphate. The carbonate solution was slightly acid, and gave a precipitate on boiling; the filtrate was not acid, and was free from phosphate.

11. The reaction of water in which barley has been steeped is slightly acid, and its colour orange, or deep orange-yellow. Such water gives a white precipitate with hydric metaphosphate* in the cold, and the filtrate yields a further precipitate on boiling.

Water containing calcic sulphate was found to have taken up less colouring water than distilled water, and to be lighter when more calcic sulphate was present. One of the gypsum water extracts, when heated to boiling, gave far less precipitate than the aqueous extract. It furnished no precipitate in the cold with hydric metaphosphate.

12. Although the amount of organic constituents extracted from barley is small, seldom exceeding four-tenths per cent., we cannot consider it unimportant. In the chemistry of minute quantities we repeatedly find vast qualitative effects arising from the presence of small masses, and depending sometimes for their very occurrence on the condition that the masses are small. May not the absence, at a critical time in the life of the sprouting plant, of a little or all of its most soluble albuminoid, materially affect the quality of the resulting malt; when even so apparently indifferent a circumstance as the mode of supplying air to the plant produces a marked alteration of character?

Inferences and Remarks.

It is obvious from the experiments recorded in (11) that water in which barley has been steeped contains at least two albuminoid bodies, one of which is thrown down by metaphosphate in the cold, the other on boiling. The former of these can be wholly kept back within the grain by the action of a gypsum solution, and probably, but with rather less efficiency, by a chalk solution.

13. The results given in the Tables show that one general effect of a calcic solution is to keep back nitrogenous matter within the grain;

* This reagent, which has been for several years employed by one of us as an extremely delicate reagent for albumin, is prepared as follows. A quantity of sodic metaphosphate (Maddrell's) is covered with strongly acetified water, set aside, and occasionally shaken. The clear liquid, which must always be kept over the undissolved sodic salt, constitutes the reagent. The metaphosphate has the great advantage over the nitrate of not decomposing albumin when boiled therewith.

but the strongest solutions ever likely to be employed in malting are far from entirely preventing the escape of nitrogenous matter.

If we glance also at the "nitrogen" as compared with the "extracts," we cannot fail to perceive that the greater part of the extracts is made up of non-albuminous bodies. In most cases, the stronger the steep-water is in saline constituents, the greater is the amount of extract withdrawn, and the less the amount of albuminoid matter allowed to escape.

14. In comparing Table VI with Table V, it will be found that the mineral constituents in Water A probably counterbalance each other's effects, so that, on the whole, Water A acts like distilled water. Water B very closely resembles Water A as to extract; but when compared with distilled water, it is seen to take out less nitrogen.

If we have regard to temperature, it is probable that the Burton water takes out more nitrogen than, and at least as much extract as, either gypsum or chalk solution, or waters resembling the Burton sample in (1), gypsum + common salt, or (2), chalk + common salt. The special esteem in which the Burton sample is held may therefore be due to its nitrate, which is well known to have a highly stimulant action in the germinating of malt—a process which demands much oxygen.

15. The practical value of our experiments will depend very much upon the view taken by maltsters as to the propriety of locking up, as far as possible, both the non-albuminous and albuminous matters of the grain. Opinions as to the employment of hard or soft waters are at present very much divided. For our own part, we lean to the belief that the healthy germination of the seed will be best promoted by keeping within it as much as possible of its natural constituents, as is done in ordinary processes of agricultural growth. We have, however, shown that the usually available reagents for this purpose, if employed in the concentrated form, take out more extract; if in the diluted form, more albumin. The proper compromise, then, will be to select a reagent of medium strength; and the best at present known to us is a gypsum solution containing about one-tenth per cent. It would be easy, and probably advantageous, to add to this such a proportion of calcic nitrate as would correspond to a few tenths per 100,000 of nitric nitrogen. Finally, the question naturally occurs, Why not use sufficient water just to saturate the grain, and no more? If this plan were adopted (and we are unaware of any practical difficulties in the way), the softest natural water might be employed with success, and not a trace of its constituents would be lost, as in the best existing practice, to the germinating grain.

IX.—RESEARCHES ON THE RELATION OF THE MOLECULAR STRUCTURE OF CARBON COMPOUNDS TO THEIR ABSORPTION-SPECTRA.

By W. N. HARTLEY, F.R.S.E., &c., Professor of Chemistry, Royal College of Science, Dublin.

Part VI. *On the Constitution of Pyridine, Picoline, Quinoline, and Cyanuric Acid.*

WHEN an atom of carbon is united to an atom of nitrogen, no absorption-bands are seen in the ultra-violet spectra transmitted by such a combination. This conclusion may be drawn from the experiments of M. Soret and of the late Dr. W. A. Miller, who proved the photographic transparency of hydrocyanic acid and the cyanides.

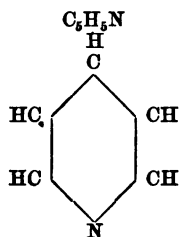
I have considered it necessary to make independent observations, on account of the more delicate nature of the instrument and the photographic process I employ, and because it is necessary to take into consideration the quantity of substance in the various solutions examined.

A strong solution of hydrocyanic acid was prepared by distilling potassic ferrocyanide in the usual way with dilute sulphuric acid; this was redistilled and its strength determined with a volumetric silver solution. It contained 11.9 per cent. of HCN.

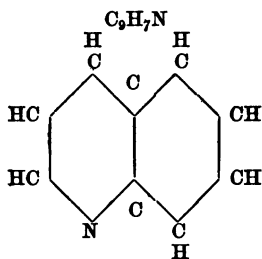
The liquid was examined in the undiluted state in layers 30 mm. and 15 mm. in thickness, and subsequently in various degrees of dilution. Hydrocyanic acid is a remarkably diactinic substance, and does not under any ordinary circumstances exhibit absorption-bands. Hence we may draw the conclusion that—

The simple union of carbon to nitrogen does not cause selective absorption of the ultra-violet rays.

It has been suggested, and it is generally believed, that pyridine and its homologues are compounds in which an atom of triad nitrogen replaces an atom of carbon in a closed chain of six atoms. Koerner's formula for quinoline represents it as naphthalene in which an atom of carbon in one of the benzene nuclei is replaced by triad nitrogen, and moreover the recent synthesis of quinoline by Baeyer has confirmed this theory of its constitution (*Ber.*, 12, 1320). Without committing ourselves to views as to the internal structure of the molecules, we may write the two substances thus:—



Pyridine.



Quinoline.

As already shown, if a molecule contains only two pairs of carbon-atoms doubly linked, it will show no absorption-bands, and it is conceivable that if a carbon-atom be replaced by nitrogen, as in the formulæ given above, the nature of the absorption will not be materially affected by this modification, because the structure of the nucleus of the compound is unaltered; and although there is one atom of hydrogen less in the molecule, we know that the addition of hydrogen-atoms, provided they do not interfere with the structure of the nucleus, has no effect on the absorption, so that we may expect the withdrawal of one atom to have as little influence. In fact we should expect to see a banded spectrum whatever element might be introduced into the benzene nucleus, if the atom were capable of vibrating in unison with the carbon-atom it has replaced.

Likewise if we regard picoline and the two pyridine-dicarboxylic acids as modifications of the pyridine nucleus drawn above, and standing in the same relation to it that toluene and the phthalic acids occupy with regard to benzene, we should expect them also to exhibit absorption-bands.

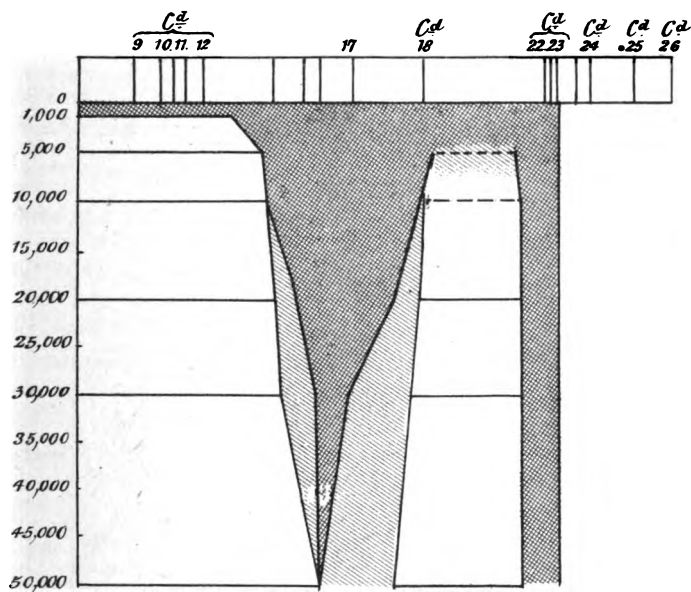
Quinine shows a remarkable banded spectrum, which is probably due to the conjugation of four pyridine or two quinoline nuclei, since Dobbie and Ramsay (*Chem. Soc. J.*, 1878; 1879, p. 189) have obtained two pyridine-dicarboxylic acids and pyridine-tricarboxylic acid by the oxidation of this alkaloid. Samples of the two former substances were kindly given to me by Dr. Ramsay, and also some di-pyridine and picoline. Particulars regarding the spectra of these substances are the following:—

α-Pyridine-dicarboxylic Acid. — The substance was dissolved in absolute alcohol, and solutions containing 1000, 5000, 10000, 50000, and 100000 were examined. A strong band of absorption was noticed, which was not extinguished even in the weakest of these solutions. The band is most strongly marked at a dilution of 1 in 20,000; it lies between the lines 17 and 18 Cd, wave-lengths 2743·4 and 2,574·2, Diagram X.

β-Pyridine-dicarboxylic Acid. — The solutions in absolute alcohol

DIAGRAM IX.

δ. PYRIDINE-DI-CARBOXYLIC ACID.

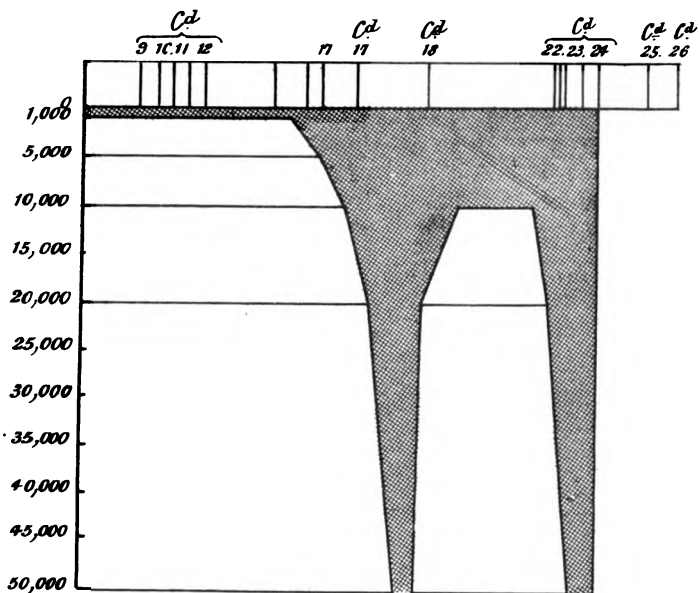


Scale. 10,000 parts to half an inch.

DIAGRAM X.

α . PYRIDINE-DI-CARBOXYLIC ACID.

Numbers indicating the position of cadmium lines of known wave length.

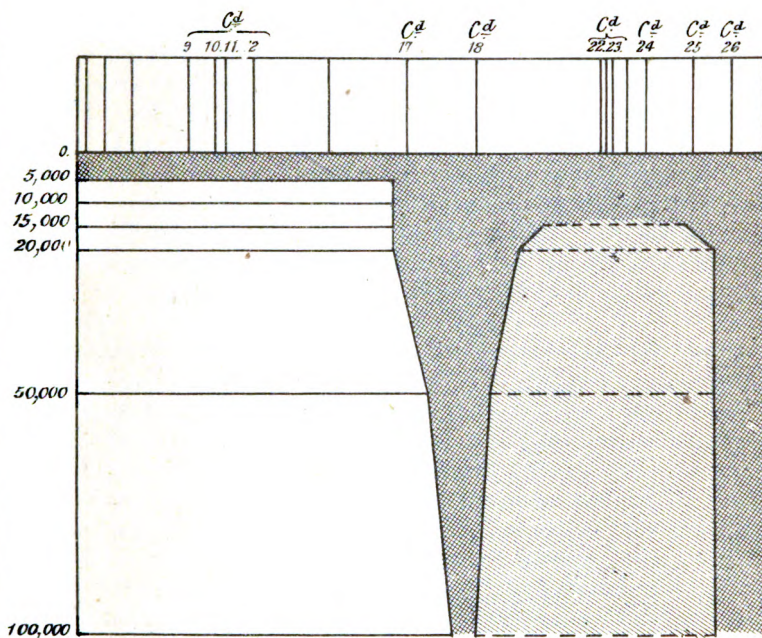


Scale.: 10,000 parts to half an inch.

DIAGRAM XI.

P I C O L I N E .

Numbers indicating the position of cadmium lines of known wave length.



Ordinates = volumes of solution containing one volume of Picoline.

Scale. 20,000 parts to half an inch.

examined contained $\frac{1}{1000}$, $\frac{1}{2000}$, $\frac{1}{3000}$, $\frac{1}{4000}$, $\frac{1}{5000}$, and $\frac{1}{6000}$ of their weight of the substance. There was a considerable absorption, though not of great intensity, in this last liquid, the bands stretching from below 17 to 18 Cd. The band of transmitted rays did not extend as far as 22 Cd, while in the previous case they went up to 23 Cd, Diagram IX.

Picoline.—Solutions in absolute alcohol containing $\frac{1}{1000}$, $\frac{1}{2000}$, $\frac{1}{3000}$, $\frac{1}{4000}$, and $\frac{1}{5000}$ of the substance were examined. The solution containing $\frac{1}{1000}$ shows a strong absorption-band lying beyond 17 Cd, but a broad band of rays is faintly transmitted further on. Solutions containing $\frac{1}{2000}$ show a strong absorption-band lying between 17 and 18 Cd, and a band of transmitted rays, which, however, are faint, between 18 and 25 Cd. The absorption-band is narrowed but not destroyed by dilution to $\frac{1}{3000}$, and the transmitted rays are still faint. As this substance is a methyl-pyridine, it affords us direct evidence of the fact that the substitution of N for carbon in the benzene nucleus does not interfere with the selective absorption, but only modifies it in some degree. The chief modification is seen in the greatly increased intensity of the absorption.

By comparing the Diagram XI with that representing the absorption of methyl-benzene (*Phil. Trans.*, 1879, Pl. 25) a very close and striking resemblance is noticed, but with the following differences:—the narrow band of transmitted rays, which is a little more refrangible than 17 Cd, and appears to be characteristic of benzene hydrocarbons, is absent from the picoline spectrum, and the broad and similar band of faintly transmitted rays which appears first in solutions containing 1 part of toluene in 2,000 of alcohol does not become visible until a dilution of 1 in 15,000 in the case of picoline. And whereas a dilution of 3,000 times extinguishes a distinct absorption-band in the case of toluene, the similar band of picoline is continued to a dilution of 1 part of the substance in 100,000 of liquid.

Quinoline.—The pure substance was obtained by fractionating a specimen purchased from Messrs. Burgoyne and Burbidges; the portion distilling between 235° and 240° was regarded as the purest. Its identity was established and its purity determined in the following manner. Hydrochloric acid gas was passed into a portion of the quinoline until it solidified on cooling into a hard crystalline mass. This hydrochloride was dissolved in water, and a solution of platonic chloride was added. The platinoquinoline hydrochloride precipitated was washed by decantation, separated by filtration, and again washed until free from platonic chloride, then dried at first at a temperature not exceeding 80°, and finally heated for a short time to 100°. A weighed portion of the compound was then ignited, and the residual platinum determined.

	Weight of substance. gram.	Weight of platinum. gram.	Per cent. Pt.
I.....	0.7516	0.2192	29.16
II.....	0.8008	0.2326	29.04

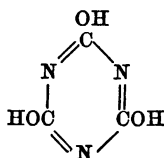
The theoretical quantity of platinum in the salt is 29.44 per cent.

Photographs were taken of solutions of the base in alcohol. The solutions contained $\frac{1}{10000}$, $\frac{1}{5000}$, $\frac{1}{1000}$, $\frac{1}{100}$, $\frac{1}{10}$, $\frac{1}{1000}$, $\frac{1}{100}$, and $\frac{1}{10000}$ their weight of the substance.

One narrow band of absorption is seen just a little beyond 12 Cd in solutions containing $\frac{1}{10000}$. Two narrow bands and a broad one are seen in solutions containing $\frac{1}{1000}$, and traces of absorption continue until the dilution has reached $\frac{1}{50000}$.

It is interesting to compare the quinoline, Diagram XII, with the naphthalene, Diagram III (*Chem. Soc. J.*, 1881). Two of the four absorption-bands have become fused, and the remaining ones are much lowered in refrangibility; at the same time the intensity of the absorption is decreased. Thus three strong bands are seen in solutions containing 1 part of substance in 100,000 of a solution of naphthalene, but with a dilution of 1 in 50,000 they have all disappeared in the case of quinoline.

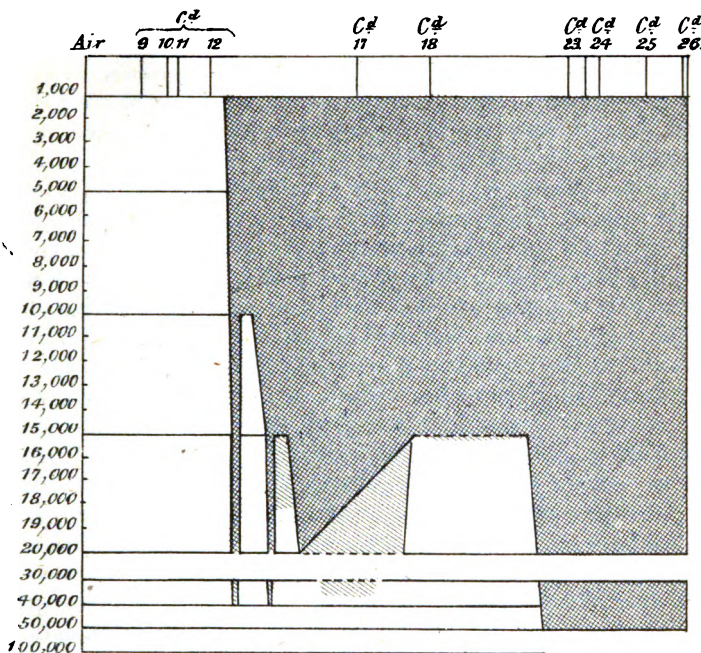
From the ease with which cyanic acid becomes converted into cyanuric acid, evolving a considerable amount of heat during the change, and on account of the necessity for the absorption of a large amount of heat to effect its decomposition into the simpler molecule, it appears highly probable that the carbon and nitrogen-atoms constitute a closed chain, forming a compound which may graphically be represented thus:—



Such an atomic grouping would probably be the cause of absorption-bands, the hydroxyls in the molecule, however, being inactive in this respect, as I have shown by previous observations (*see No. II, April, 1881, this Journal*).

In order to gain some knowledge of the constitution of cyanuric acid a beautifully crystallised specimen was dissolved and the ultra-violet spectrum was submitted to its action. A solution of 1 part by weight in 200 of water gave a strong absorption-band, stretching from wave-length 2687 to about 2630, an interval lying midway between 17 and 18 Cd. The band of rays beyond this, which was but faintly transmitted, does not extend to 22 Cd. A solution con-

DIAGRAM XII.
QUINOLINE



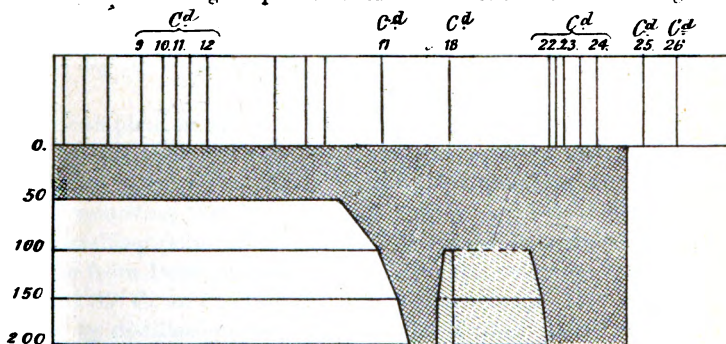
Absorption bands traceable in solutions containing $\frac{1}{1000}$ of the substance.

Thickness of layer of liquid = 15 mm.

Ordinates = proportion of alcohol to one part by weight of Quinoline.

DIAGRAM XIII.
CYANURIC ACID.

Numbers indicating the position of cadmium lines of known wave length



Ordinates = The proportion of liquid containing one part by weight of the substance.

Scale. 100 parts to half an inch. 1 in 2,000 transmits all rays.

taining 1 part of substance in 2,000 of water is quite diastinct. The presence of the absorption-band proves, I think, that there is a union between the 6 atoms of nitrogen and carbon similar to that suggested by the graphic formula given above, because otherwise the carbons and nitrogens would stand to each other in the same relation that obtains in hydrocyanic acid, which is a perfectly diastinct substance.

Judging from the evidence afforded by the study of carbon compounds, the account of which has been given in my former papers, it is not at all likely that the carbon-atoms in cyanuric acid can be only singly linked; at the same time the union of the atoms cannot be of so intimate a nature as that occurring in benzene, because its actinic absorption is so much less powerful. It appears therefore that this substance possesses a nucleus with a compactness of structure intermediate between that of benzene hexachloride and that of benzene. Now as the atoms of the nucleus in the first body are singly linked, if we accept the justifiable conclusion that those in cyanuric acid are alternately doubly linked, it would appear probable that in benzene each carbon-atom is united with other three carbons, since this is the only manner in which a more compact atomic linking than that expressed in the formulæ of benzene hexachloride and cyanuric acid can be made consistent with the perfect symmetry of the compound, or in other words, with the perfect equality of function of the six carbon-atoms.

X.—On Peppermint Camphor (*Menthol*) and some of its Derivatives.

By R. W. ATKINSON, B.Sc. and H. YOSHIDA.

PEPPERMINT camphor, as found in commerce, even when not expressly adulterated with magnesium sulphate, is almost invariably contaminated with oily matter, which accompanies it in the plant, and on account of the difficulty of removing this impurity, most of the previous determinations of the melting point are too low. The specimens upon which we worked came from Dewa, in the north of Japan, and were found to melt at about 35° C., and to boil at 210—211° (uncorr.). This menthol was purified by distillation, the first and last portions being rejected, after which the cooled and solidified product was well pressed between filtering paper, and exposed repeatedly in thin layers to the air. By several repetitions of this process the melting point was finally raised to 42·2°, the solidifying point to 40·3°, and the boiling point to

212° (corr.). These numbers agree most nearly with those of Beckett and Wright (*Chem. Soc. J.*, 1876, 1, 1). The melting points were determined by enclosing the capillary tube, containing the menthol, together with a delicate thermometer, in a test-tube immersed in water, which was slowly heated, a process originally described by Anschütz and Schultz (*Ber.*, 10, 1800).

MENTHONE, $C_{10}H_{18}O$.

Mr. Moriya has shown (*Chem. Soc. J.*, 1881, Trans., 77) that when menthol is heated in sealed tubes with acid bichromate solution at 120°, for about 10 hours, an oil boiling at 204—205° is obtained, having a composition which agrees with the formula $C_{10}H_{18}O$. We have repeated this experiment, preparing larger quantities, and have made determinations of some of the principal physical properties of the compound, believing that this knowledge will be of assistance in elucidating the structure of the menthol derivatives.

Weak chromic acid liquor has very little action upon menthol at 100°. To prepare menthone, about 30 grams of purified menthol were placed in a narrow-necked bottle, together with 10 grams of potassic dichromate, and about an equal weight of sulphuric acid; on shaking the mixture much heat was liberated, and the menthol was changed into a black spongy mass. The bottle was then heated in a digester to a temperature of 135°, for about four hours. At the end of that time the light oily layer was separated from the solution of chromic sulphate, and subjected several times to the same treatment with fresh oxidising mixtures. The optical activity of the oil was examined after each treatment, and it was observed that it gradually decreased from -59° to 0° for the transition tint, but did not stop there, the rotation becoming positive and increasing till it rose to $[\alpha]_D = +21^\circ$.

Purified by distillation, menthone is a colourless mobile liquid, neutral to test-papers, soluble in almost all proportions in alcohol, chloroform, benzene, and carbon disulphide, but insoluble in water.

On combustion the following numbers were obtained :—

	(1.) 0.5918 gram gave 1.6884 gram CO_2 and 0.6296 gram H_2O .				
	(2.) 0.4362	„	1.2415	„	0.4625
	(3.) 0.3472	„	0.9902	„	0.3659
	1.	2.	3.	Mean.	Theory
Carbon	77.81 p.c.	77.62 p.c.	77.78 p.c.	77.73	$C_{10}H_{18}O$. 77.92
Hydrogen	11.82 „	11.78 „	11.71 „	11.77	11.69

Mr. Moriya's numbers (not published in his paper) were—

	Mean.
Carbon	77.59 per cent.
Hydrogen	11.87 ,,

Two determinations of the vapour-density of the compound gave the numbers 77.45 and 76.69, the number calculated for $C_{10}H_{18}O$ being 77.0.

Menthone boils at 206.3° (corr.), and smells like much diluted peppermint. It does not combine with acid sodium sulphite; concentrated oil of vitriol has scarcely any action on it in the cold.

When menthone is repeatedly cohobated with zinc chloride, a hydrocarbon is obtained, which smells like that of the hydrocarbon to be afterwards described, obtained from menthol by the action of hydric iodide with subsequent treatment with caustic soda and sodium. A pasty somewhat opalescent mass is formed from which the oil is liberated by treatment with water. The amount of the hydrocarbon obtained was, however, too small to permit of its identification; it was probably a mixture of several bodies.

That menthone stands to menthol in a similar relation to that in which camphor stands to borneol, is shown by the fact that menthol can be reproduced from its ketone, $C_{10}H_{18}O$, by a reaction quite similar to that by which borneol is produced from camphor. When a solution of menthone in petroleum of somewhat high boiling point, is heated with metallic sodium, the latter is quickly dissolved; and on decomposing the solution by carbonic acid, shaking up the product with water, rapidly separating the water from the oily layer, and setting it aside, it deposits minute crystals of peppermint camphor, which can be obtained in a coherent mass, best by distilling in a current of steam. When purified by the process adopted for the natural menthol, it was found to melt at 42.2° , solidifying at 40.3° , but to have a less energetic laevorotatory power than the natural product, viz., -39° . It may be remembered that synthesised borneol differs in its specific rotatory power from the natural substance, but the present instance is perhaps more remarkable, seeing that the intermediate body possesses a rotation opposite both to the natural and to the artificial menthol.

Specific Rotatory Power.—Not having at our command any other kind of polarimeter, we were obliged to be content with the results given by a Soleil-Ventzky saccharimeter, although, as is well known, its indications are not exact for other substances than sugar.

Mr. Moriya (*loc. cit.*) stated that this body was inactive to polarised light, but as his experiments were made upon solutions of the oil, which further was probably not completely freed from menthol, the rotatory effect was imperceptible. We found that the pure oil in a decimeter tube gave an average rotation of 49.73 divisions, from which the specific rotatory power is calculated.

$$[\alpha]_j = + \frac{49.73 \times 38.34}{100 \times 0.901} = + 21.16^\circ.$$

Specific Gravity and Rate of Expansion.—The specific gravity was determined by the use of a carefully calibrated specific gravity bottle, and the weights reduced to a vacuum; the numbers give the density at the temperature mentioned, compared with that of water at 4° C. Each number is the mean of five experiments.

Temperature.	$D_{\frac{t}{4}}$	Volume.
0°	0.9126	1.00000
10	0.9048	1.00862
20	0.8972	1.01716
40	0.8819	1.03481
60	0.8665	1.05320
80	0.8511	1.07226
100	0.8355	1.09228

When combined, these numbers lead to the formula for the expansion—

$$V_t = 1 + 0.00085037t + 0.0000004156t^2 + 0.0000000031415t^3.$$

Molecular Refraction.—The refractive index was determined with the aid of a delicate spectrometer belonging to the physical laboratory of the University of Tôkiô, and fully described by Prof. Mendenhall* in the Eighth Memoir of the Science Department of the University ("On the Wave-lengths of some of the Principal Fraunhofer Lines).

The sources of light employed were the red and green lines of the hydrogen spectrum having the wave-lengths 6562 and 4682 respectively. The temperature of the air at the time of the observations was 8—9°, and the specific gravity of the liquid at 8.5° was 0.90602.

$$\begin{array}{ll} \text{The index of refraction for } H_a = 1.45283 \\ \text{,, ,, ,, } H_g = 1.46094 \end{array}$$

Using Cauchy's formula for an infinite wave-length (Brühl, *Annalen*, 200, 139, we get—

$$\begin{array}{l} A = 1.442998 \\ B = 0.425268 \end{array}$$

The molecular refraction is, therefore,

$$R = P \left(\frac{A - 1}{d} \right) = 154 \left(\frac{1.442998 - 1}{0.90602} \right) = 75.3.$$

Using the values given by Brühl for carbon, hydrogen, and oxygen, the calculated molecular refraction for $C_{10}H_{18}O$, the carbon-atoms not

being doubly combined, is 75.1, a result agreeing so well with the observed number, that we may conclude that the carbon-atoms are all singly united.

MENTHENE, $C_{10}H_{18}$.

This substance was prepared by heating menthol with zinc chloride. The purified peppermint camphor was cohobated with about twice its weight of zinc chloride, in a flask provided with a vertical condenser. After heating for about half a day, the hydrocarbon was separated and then digested with sodium for some time at a gentle heat. The product was carefully fractionated several times, and the main portion which passed over at 165–166° (uncorr.) was preserved for examination. It was found necessary to purify it from small quantities of polymerised bodies, and for this purpose the liquid was digested with clean pieces of sodium, and occasionally separated by distillation from a reddish-brown precipitate. After about a month the production of the reddish precipitate ceased; the liquid was again fractionated; and that portion which distilled at 167.4° (corr.) served for the following determinations:—The observed boiling point, 167.4°, is higher than that usually given for menthene, but the greater part of the product obtained distilled constantly at that temperature.

Specific Rotatory Power.—At 15° the liquid contained in a tube 1 decimeter long, gave a rotation equal to 10.73°, the specific gravity at the same temperature being 0.8102, and the specific rotatory power $[\alpha]_D^{15} = +13.25^\circ$. This observation differs from that of previous observers, who have regarded menthene as an optically inactive body. In Mr. Moriya's case this was perhaps caused by the menthene used containing a little unaltered menthol, as well as from the circumstance that he used dilute alcoholic solutions, whilst the above determinations were made with the undiluted liquid.

Specific Gravity and Rate of Expansion.—The specific gravity at the various temperatures was determined, as in the case of menthone, each number being the average of five experiments.

Temperature.	D_{40}^t	Volume.
0°	0.8226	1.00000
10	0.8145	1.00994
20	0.8073	1.01899
40	0.7909	1.04008
60	0.7761	1.06000

These results lead to the formula for the volumes—

$$V_t = 1 + 0.00099183t + 0.000000592t^2 + 0.000000075t^3.$$

Molecular Refraction.—The indices of refraction were found to be—

$$\begin{aligned} &\text{for } H_a = 1.448997 \\ &\text{and for } H_b = 1.459200. \end{aligned}$$

from which we find—

$$\begin{aligned} B &= 0.534289 \\ A &= 1.43664 \end{aligned}$$

The specific gravity at 8.5° is 0.8137: hence the molecular refraction is—

$$R = 138 \times \frac{1.43664 - 1}{0.8137} = 74.045.$$

The number calculated for $C_{10}H_{18}$ from the values for carbon (in single union) and hydrogen given by Brühl, is 71.82. A closer agreement is obtained by assuming the existence of one pair of carbon-atoms doubly united, the rest being in single union, viz.,—

$$C''_2 + C'_8 + H_{18} = 73.82.$$

Menthene is a colourless mobile liquid, of an agreeable odour, recalling that of cymene; moderately soluble in ether or alcohol, more so in benzene, turpentine, and petroleum. When heated with fuming hydrochloric acid for some time it yields hydrochloride of menthene, $C_{10}H_{18}Cl$, an oil more or less coloured yellow, which after washing with water and drying over potassic carbonate, contained, in two experiments, 20.25 and 20.3 per cent. of chlorine, the theoretical percentage being 20.34.

Heated with hydriodic acid at the ordinary pressure of the air, menthene takes up the elements of the acid, forming an unstable brown oil, having an odour resembling that of the iodide formed by the action of hydriodic acid on menthol.

ACTION OF HYDRIODIC ACID ON MENTHOL.

About 10 oz. of hydriodic acid solution, of sp. gr. 1.7, were heated with about 6 oz. of menthol in a flask with an inverted condenser; the heating was continued for three days, at the end of which time the dark oily liquid was separated from the aqueous portion. The oil decomposes on distillation between 170° and 200° . The distillate was lighter than water, and had a pleasant odour; when it was boiled with caustic soda solution, the dark colour which it assumed on standing, by the decomposition of some iodo-compound, was removed; but again on standing the dark colour reappeared. Nothing distilled below 160° : hence no decane was present. Berthelot (*Bull. Soc. Chim.*, 11, 102) states that a small quantity of amyl hydride and of decyl hydride, together with terpine hydride ($C_{10}H_{20}$), which formed

three-fourths of the total liquid, are produced in this reaction. The strength of the hydriodic acid used in his experiments was, however, higher than in ours.

When the above liquid is cohobated with caustic soda-solution, then with sodium, and distilled, it yields a clear colourless hydrocarbon of an agreeable odour. It polymerises on heating, and can only be purified by long digestion with sodium. The corrected boiling point was found to be 168.6° . Combustion showed that it consisted mainly of a hydrocarbon, $C_{10}H_{16}$, mixed with a small quantity of a more highly hydrogenised body, $C_{10}H_{18}$, or $C_{10}H_{20}$.

- (1.) 0.3642 gram gave 1.1714 gram CO_2 and 0.3989 gram H_2O .
 (2.) 0.4212 " 1.3517 " " 0.4769 "
 (3.) 0.4034 " 1.3024 " " 0.4400 "

	1.	2.	3.	Mean.
Carbon	87.72 p.c.	87.52 p.c.	88.05 p.c.	87.76
Hydrogen ..	12.17 "	12.58 "	12.12 "	12.29
				<hr/> 100.05

	Calculated for	
	$C_{10}H_{16}$	$C_{10}H_{18}$
Carbon	88.235	86.96
Hydrogen ..	11.765	13.04
	<hr/> 100.000	<hr/> 100.00

Two determinations of the vapour-density made with Victor Meyer's apparatus, gave the numbers 66.1 and 68.4; mean 67.25. The number calculated for $C_{10}H_{18}$ is 68.0.

Specific Rotatory Power.—As a mean of five observations, the liquid contained in a decimeter tube was found to rotate the ray of polarised light through 4.23° : hence, density at $18^{\circ} = 0.8137$,

$$[\alpha]_D = \frac{4.23}{0.8137} = + 5.2^{\circ}.$$

Specific Gravity and Rate of Expansion.—The specific gravity was determined as before.

Temperature.	D_4^t	Volume.
0°	0.8254	1.00000
10	0.8178	1.00929
20	0.8111	1.01763
40	0.8001	1.03162
60	0.7924	1.04165

These numbers lead to the following equation, expressing the volumes at different temperatures:—

$$V_t = 1 + 0.000976768t - 0.00000479t^2 + 0.00000000133t^3.$$

Molecular Refraction.—The indices of refraction were found to be for $H_a = 1.4481614$, and for $H_b = 1.457148$, from which we find—

$$A = 1.43723$$

$$\text{and } B = 0.47059$$

The specific gravity at 18° being 0.8115 , the molecular refraction for $C_{10}H_{16}$ is $R = 136 \times \frac{1.43723 - 1}{0.8115} = 73.28$.

The number calculated for $C_{10}H_{16}$, all the carbons being in single union, is 69.24 , but if we assume the presence of two pairs doubly united, we get the number—

$$C'_6 + C''_4 + H_{16} = 73.24.$$

This hydrocarbon is a clear, colourless, mobile liquid, easily soluble in petroleum or benzene, less so in ether and alcohol, and insoluble in water. Its odour resembles that of cymene. Bromine acts strongly upon it, about two atoms being taken up, with evolution of some hydrobromic acid; the resulting bromo-compound is as unstable as the iodo-compound.

XI.—On some Higher Oxides of Manganese and their Hydrates. Part II.

By V. H. VELEY, B.A., F.I.C., Christ Church Laboratory, Oxford.

Preliminary Discussion.

It seemed to the author that a continuation of the investigations on the higher oxides of manganese and their hydrates (cf. this Journal, 1880, 581—592) might throw some further light on the constitution of these compounds. Experiments have recently been published on the oxides of manganese by Wright, associated with others (this Journal, 1880, 775—785), Moissan (*Ann. Chim. Phys.* [5], 21, 199—255), and Pickering (*Chem. News*, 43, 189 *et seq.*); these researches will be alluded to in the course of the present communication.

Purity of the Oxides.

As considerable stress was laid in the former communication on the

probable difference of behaviour of the higher oxides when pure, and when contaminated with alkali, a spectroscopic analysis was made of the samples used. The method of procedure was as follows:—A strong solution was prepared by dissolving 1.358 grams of the hydrated oxide in 20 c.c. concentrated hydrochloric acid. A drop of this solution introduced on a platinum wire into a Bunsen burner, and the flame viewed through a double prism spectroscope, gave a spectrum in which the presence of no metals other than manganese and sodium was indicated. In order to determine the maximum amount of impurity of potassium, two flasks, A and B, were taken, in the former of which were placed 10 c.c. concentrated hydrochloric acid (prepared from ammonium chloride and sulphuric acid), and in the latter the same volume of hydrochloric acid containing a known weight of the hydrated oxide in solution. To the former was added a dilute solution of potassium chloride, a cubic centimeter at a time, until a drop taken up on a platinum wire gave distinctly the red line K_{α} . The experiment was then repeated with flask B, and it was found to require exactly the same number of c.c. before the line K_{α} became visible. Hence the amount of impurity of potassium is less than the amount contained in 1 c.c. of the dilute potassium chloride solution. By this process it was shown that the manganese chloride solution contained less than 1 part of 1,000 of potassium chloride. (Further corroborative evidence of the absence of potash was afforded by the readiness with which the oxides were reduced in hydrogen, and the freedom from so-called spontaneous oxidation of the manganese monoxide formed.) The experiment described above was repeated, a calcium chloride (from Iceland spar) being substituted for the potassium chloride solution. Owing to the close proximity of the red and green lines, Ca_{α} and Ca_{β} with Mn_{α} and Mn_{β} , observations were made with the yellow calcium lines on either side of the sodium line; or on moistening the wire after the experiment with dilute hydrochloric acid the calcium spectrum could be obtained free from that of manganese. (This is probably due to the retention of the lime by the oxide of manganese as calcium manganate, which is less readily dissolved by the hydrochloric acid, and so is volatilised after the greater part of the manganese passed off.) By this it was shown that the chloride of manganese contained less than 1 in 6,800 of calcium chloride. The apparatus and the methods of analysis employed have already been described (*vide supra*).

Changes produced when the Higher Oxides are Heated in Nitrogen.

Nitrogen was chosen in order to study the dehydration of the peroxides at increased temperatures in an atmosphere free from oxygen,

whereby the loss of water is not accompanied with, or affected by, any secondary chemical reaction. The nitrogen gas was prepared by aspiring over red-hot metallic copper air purified from carbonic acid, and mixed with ammonia by passing through a strong solution of the gas. By so regulating the air and ammonia current, that only one part of the copper is oxidised, while the other part is unaltered, the nitrogen is obtained free from oxygen and hydrogen, with one or other of which it would be contaminated if the contents of the heated tube were completely oxidised or completely reduced. (This ready method of obtaining pure nitrogen is not described in any of the more recent text-books, and was first adopted by Harcourt.)

Before the gas entered the drying and purifying apparatus, it was passed through a considerable length of red-hot combustion tubing filled with copper foil and cupric oxide, and then through a washing bottle containing alkaline pyrogallate.

Before commencing the experiments fresh analyses were made of the hydrated peroxide used in the former publication, the method of preparation of which has already been described at length.

	Mean of values obtained.	Values obtained in former experiments.
Manganese monoxide	75.34	75.37
Oxygen	14.28	14.06
Water	10.40	10.54
	100.02	99.97

These analyses are fairly accordant, and agree with the hypothesis that it is an oxide of formula Mn_2O_{11} of not very definite hydration.

A series of experiments were then made to ascertain whether the composition of the oxide when heated in nitrogen from 60—200°, remains unchanged so far as regards the relation of manganese monoxide to available oxygen, or whether the loss in weight is solely attributable to the loss of water of hydration.

Remarks on Table I.

I. The temperatures at which stable hydrates seem to be formed are 90—95° and 170—180°.

II. Throughout the experiments there is no marked difference between the loss in weight of the oxide and the water collected in the drying tube. This shows that the oxide when heated in nitrogen from 180—200°, loses only water of hydration, and not available oxygen. (In the experiments marked ‡ there was slightly more water collected

TABLE I.—Continuous Series in Nitrogen.

Condition.	Time.	Temp.	Weight of oxide.	Loss.	H ₂ O coll.	D*.	Flow of gas.†	Remarks.
Heated in a current of nitrogen ..	2 hours	80—81°	0.5772 gram	0.0247 gram	0.0245 gram	—	575 c.c.	
Ditto	"	89—90	0.5525 "	0.0023 "	0.0021 "	—	375 "	
Ditto	"	89—90	0.5502 "	0.0007 "	0.0010 "	+	300 "	Mn ₂ O ₁₁ ·2H ₂ O.
Ditto	"	95	0.5495 "	0.0031 "	0.0034 "	+	500 "	
Ditto	"	105	0.5466 "	0.0016 "	0.0021 "	+	500 "	
Ditto	"	115	0.5450 "	0.0032 "	0.0033 "	+	500 "	
Ditto	"	124	0.5418 "	0.0020 "	0.0022 "	+	500 "	
Ditto	"	130	0.5398 "	0.0018 "	0.0046†	+	500 "	
Ditto	"	140	0.5364 "	0.0016 "	0.0020 "	+	500 "	
Ditto	"	150	0.5356 "	0.0008 "	0.0043†	+	500 "	
Ditto	"	160	0.538 "	0.0028 "	0.0030 "	+	460 "	
Ditto	"	170	0.5318 "	0.0010 "	0.0020 "	+	500 "	Mn ₂ O ₁₁ ·H ₂ O.
Ditto	"	180	0.5318 "	nil	0.0006 "	nil	500 "	
Ignited in a current of air	1½ hours	low redness	0.4844 "	0.0474 "	0.0183 "	—291	500 "	Mn ₂ O ₃ .
Ditto	"	do.	0.4844 "	nil	nil	nil	550 "	
Ignited in a current of hydrogen..	"	bright redness	0.4834 "	0.0510 "	—	—	—	MnO.
Ditto	"	do.	0.4834 "	nil	—	—	—	

* D = difference in decimilligrams.

† The numbers in column VIII show the rate of flow of gas in c.c. per hour; they can only be regarded as approximate, being determined by the difference in level of water in the gauge of the gasometer.

TABLE II.

Condition.	Time.	Temp.	Weight of oxide.	Loss.	H ₂ O coll.	D.	Flow of gas.	Remarks.
Heated in a current of nitrogen ..	2 hours	160°	0.4256 gram	0.0319 gram	0.0319 gram	nil	600 c.c.	Mn ₂ O ₇ .H ₂ O.
Ditto	2 "	162	0.3937 "	nil	(0.0003) "	nil	550 "	
Heated in a current of oxygen....	1½ "	low redness	0.3937 "	0.0134 "	0.0014 "	— 20	550 "	
Ditto	1½ "	bright redness	0.3564 "	0.0240 "	0.0022 "	— 218	550 "	
Ditto	1½ "	do.	0.3564 "	nil	nil	nil	550 "	Mn ₂ O ₃ .
Heated in a current of hydrogen..	1½ "	do.	0.3197 "	0.0367 "	—	—	—	MnO.

TABLE III.

Condition.	Time.	Temp.	Weight of oxide.	Loss.	H ₂ O coll.	D.	Flow of gas.	Remarks.
Heated in a current of nitrogen ..	2 hours	200°	0.5046 gram	0.0391 gram	0.0389 gram	— 2	—	2(5MnO ₂ .MnO).H ₂ O.
Ditto	2 "	200	0.4655 "	0.0019 "	0.0041 "	+ 21	—	
Ditto	2 "	200	0.4626 "	nil	(0.0006) "	nil	—	
Heated in a current of air	1½ "	bright redness	0.4223 "	0.0405 "	0.0088 "	— 317	—	
Ditto	1½ "	do.	0.4224 "	nil	nil	nil	—	MnO.
Heated in a current of hydrogen..	1½ "	do.	0.3836 "	0.0388 "	—	—	—	
Ditto	1½ "	do.	0.3313 "	0.0023 "	—	—	—	

than loss in weight of oxide; these differences, amounting to 0.0065 gram, may be due either to the absorption of oxygen by the oxide when cooling before weighing, or to traces of water, not derived from the oxide, passing into the drying tube.

In order to confirm these experiments and to obviate the first-named source of error, the oxide was allowed to cool to the temperature of the room in the current of nitrogen, before it was taken out of the apparatus. By adopting this precaution, the gain in weight of the drying tube and the loss of the oxide corresponded exactly one with the other.

A third series were made in order to establish the constitution of the oxide when heated to 200°, and to corroborate the results detailed in the two tables above (I, II).

From analyses of the hydrated oxides which remained constant in weight when heated to 90—95°, 160—180°, and 200° C., in Tables I—III, confirmed by others, their constitution was determined.

Analysis of Oxide when Dried in Nitrogen at 90—95°.

	Values obtained.	Mean.	Calculated for $Mn_2O_3 \cdot 2H_2O$.
Manganese monoxide	78.67	78.67	78.58
Oxygen (by titration)	14.60—14.53	14.57	14.77
Water	6.78	6.78	6.65
	—	100.02	100.00

Analysis of Oxide when Dried in Nitrogen at 160—180°.

	Values obtained.	Mean.	Calculated for $Mn_2O_3 \cdot H_2O$.
Manganese monoxide	81.50—81.18	81.34	81.28
Oxygen (by titration)	15.21	15.21	15.28
Water	3.44—3.46	3.45	3.44
	—	100.00	100.00

Analysis of Oxide when Dried in Nitrogen at 200°.

	Values obtained.	Mean.	Calculated for $2(\text{Mn}_6\text{O}_{11})\text{H}_2\text{O}$.
Manganese monoxide	82.42—82.56	82.49	82.71
Oxygen	15.66	15.66	15.54
Water	1.75	1.75	1.75
	—	99.90	100.00

Both the latter partially dehydrated oxides readily took up oxygen at 100° C., and slowly even at 60°.*

Repetition of Experiments.

In order to confirm the former experiments it was considered desirable to repeat the whole of the research *ab initio*. A different sample of manganese chloride was purified by the processes described before, and the oxide precipitated from the acetate by a current of chlorine at 52—54°, and finally dried at 60—80°. The composition of the new sample† was found to be very nearly, but not exactly, the same as that of the former sample, the one being expressible by a formula $\text{Mn}_{24}\text{O}_{48}\text{H}_2\text{O}$, the other by a formula $\text{Mn}_{24}\text{O}_{44}\cdot 8\text{H}_2\text{O}$. This slight difference may be due to a rather greater oxidation by a longer continued action of chlorine, or to an absorption of oxygen during a protracted heating of the oxide in the air-bath. It is here only necessary to state that on repetition the former observations were confirmed in every respect. The sample B, when heated in air, went through the same cycle of changes; there were the same stopping points at which the oxide neither gained oxygen nor lost water; the absorption of oxygen began at the same temperature, and took place within the same limits; and the composition of the oxide ultimately obtained after heating to 200° was the same as that obtained by the same processes in the former experiments.

* Pickering has observed (*loc. cit.*, *supra*) a similar absorption of oxygen at 100° C. in the case of oxides prepared by different processes. He considers that the temperature at which absorption begins probably depends on the physical condition of the oxide, the quantity of so-called available oxygen, the water of hydration, and the condition to which it is exposed when heated.

† This sample will hereafter be designated sample B.

Analysis of Oxides Dried in Air at 200°.

	Mean values of second sample.	Mean values of first sample.	Calculated for $Mn_{12}O_{23}H_2O$.
Manganese monoxide	81·68	81·48	81·44
Oxygen	16·75	16·79	16·84
Water	1·65	1·69	1·72
	99·88	99·96	100·00

Action of Hydrogen.

The behaviour of the oxides of manganese when heated in a current of hydrogen has lately been made the subject of careful investigation by Wright, associated with others (this Journal, 1878, Trans., 512—527; 1880, 799—781). The author's experiments would not here be adduced did they not offer an independent confirmation of Wright's researches, though the original object in view was the possible preparation of hydrated peroxides containing less so-called available oxygen than the oxide Mn_2O_3 .

TABLE IV.—*Continuous Series in Hydrogen.*

Condition.	Time.	Temp.	Weight of oxide. Gram.	Loss. Gram.	Loss p. c.	Loss p.c. at same temp. in air.	
Heated in a slow current of hydrogen.	2 hrs.	100°	0·4192 0·4062	0·0130	3·10	2·24	
Ditto	"	110	0·4040	0·0022	3·62	2·99	
Ditto	"	120	0·4010	0·0030	4·33	3·40	
Ditto	"	130	0·3970	0·0040	5·19	3·40	
Ditto	"	140	0·3970	nil	5·19	3·85	
Ditto	"	152	0·3880	0·0090	7·44	3·85	
Ditto	"	160—170	0·3792	0·0038	9·54	4·15	
Ditto	"	180	0·3710	0·0082	11·50	4·15	
Ditto	"	190	0·3530	0·0180	15·79	4·15	
Ditto	"	200	0·3525	0·0005	15·80	4·65	
Ditto	"	200	0·3525	nil	—	—	$8(Mn_2O_3)3H_2O$

Remarks on the Table above.

I. The reduction or loss of available oxygen begins at a temperature of 130°, when there is a marked difference between the percentage loss in hydrogen and the corresponding loss at the same temperature in air; but this change is more marked at 150°.

II. The oxide constant in weight at 200° has the characteristic colour of the red oxide; the hue was peculiarly bright on first taking the oxide out of the heating apparatus, but on exposure to the air the bright surface was immediately dimmed.

This outward change is probably accompanied with an absorption of oxygen, for the oxide on keeping gained weight, and had a composition only approximate to Mn_2O_4 .

Analysis of Oxide when Heated to 200° in a Current of Hydrogen.

	Values obtained.	Mean.	Calculated for $8(\text{Mn}_2\text{O}_4)3\text{H}_2\text{O}$.
Manganese monoxide	89·90—89·70	89·80	90·35
Oxygen	7·23—7·10	7·16	6·78
Water (by difference)....	—	3·04	2·87
		100·00	100·00

In the oxide obtained the ratio of oxygen to the monoxide is $\frac{6\cdot78}{90\cdot35} \times 100 = 7\cdot97$; in Mn_2O_4 it is $\frac{15\cdot96}{212\cdot28} = 7\cdot52$.

The retention of a greater quantity of water (3·04 per cent.) by the oxide when heated in hydrogen to 200°, as compared with that retained by the oxide when heated to the same temperature in air (1·69 per cent.), oxygen (1·77 per cent.), or nitrogen (1·75 per cent.), can be explained thus: the oxide, though exposed to a current of dry hydrogen, is perpetually surrounded by the vapour of water formed by the reducing action of hydrogen on the oxide. It follows that the oxide will be dehydrated only when the tension of vapour of water emitted by it is greater than that of the water in the hydrogen atmosphere. Although the oxide was constant in weight after a second heating at 200°, yet this constant weight was attained by the removal of the oxygen absorbed by the necessary, though brief, exposure to air during the process of weighing; the formation of a small quantity of water in the cooled part of the apparatus gave, on reheating, a further proof of such absorption of oxygen by Mn_2O_4 , which has been pointed out by Dittmar, Wright, and others.

Specific Gravities of the Hydrated Oxides.

It seemed of interest to ascertain how far these hydrated peroxides of manganese, differing slightly from one another in the relative proportions of constituents, differ in their physical properties, as specific gravity.

Pure benzene was carefully dehydrated by keeping for some weeks, and subsequently distilling over sodium; the fraction which passed over between $80-81^{\circ}$ (uncorr.) was reserved for the determinations. In order to obtain as correct a value as possible for the specific gravity of the benzene, two bottles were taken and their weights compared, when filled to the mark with benzene and with water at the same temperature (16.5°), and the specific gravity of benzene was subsequently reduced to terms of water at 4° .

Specific gravity of benzene by bottle A	
compared with water at 4° C.	0.8944
Specific gravity of benzene by bottle B	
compared with water at 4° C.	0.8945
Mean	0.89445

The specific gravity of the oxides was ascertained by dropping about 1 gram of the oxide into a specific gravity bottle from a weighing tube which fitted closely to the neck of the bottle to avoid unnecessary exposure to the air. It was then covered by a layer of benzene, and warmed in a water-bath to expel air bubbles, and allowed to cool in water to the temperature 16.5° .

Specific Gravity of Sample B ($Mn_2O_3 \cdot 8H_2O$).

Two determinations were made by the method described above.

(1) Specific gravity compared with water at 4° ..	4.671
(2) " " "	4.681
Mean	4.675

Specific Gravity of the Hydrate constant in Air at 200° ($Mn_2O_3 \cdot H_2O$).

(1) Determination compared with water at 4°	4.800
(2) " " "	4.750
Mean	4.775

Specific gravity of manganese monoxide obtained by igniting the higher oxide for some days in a current of hydrogen:—

(1) Specific gravity compared with water at 4°	5.010
Former observations by Rammelsberg	5.000

As several determinations have been published by Playfair and Joule, and by Rammelsberg (*Monatsb. Ber. Akad.*, 1865, 110) of the sesquioxide and red oxide prepared by artificial processes, it was thought superfluous to repeat them.

Summary of Results.

I. The higher oxides of manganese, when heated in dry nitrogen at temperatures ranging from 60—200°, are simply dehydrated without loss of available oxygen: the dehydrated oxide formed readily absorbs oxygen.

II. The oxides, when heated in dry hydrogen, are simultaneously dehydrated and reduced; a hydrate of the red oxide is formed which readily absorbs oxygen.

III. The quantity of water retained by the peroxides, when heated to 200° in dry hydrogen, is greater than that retained by the same oxide when heated to the same temperature in air, oxygen, or nitrogen. The higher oxides and their hydrates obtained in the course of the former and present research are tabulated below, and in order to facilitate comparison, and to show their mutual relation, they are represented as oxidised products of a protoxide of molecular formula $Mn_{24}O_{24}$:—

—	$Mn_{24}O_{44}.8H_2O$	$Mn_{24}O_{45}.8H_2O$		
—	$Mn_{24}O_{44}.6H_2O$			
—	$Mn_{24}O_{44}.4H_2O$		$Mn_{24}O_{46}.8H_2O$	
$Mn_{24}O_{32}.3H_2O$	$Mn_{24}O_{44}.2H_2O$		$Mn_{24}O_{46}.2H_2O$	$Mn_{24}O_{47}.2H_2O$

In conclusion, the author wishes to express his best thanks to Mr. Vernon Harcourt for kind assistance and advice during the course of this investigation.

XII.—On a New Alkaloid from Cinchona Bark.

By DAVID HOWARD and JOHN HODGKIN.

IN investigating the alkaloids yielded by the singular bark described by Dr. Flückiger as *China Cuprea*, we have met with an alkaloid which appears peculiar to this species, and is quite distinct from that which M. Arnaud has described (*Compt. rend.*, 93, 593) under the name of *cinchonamine*, which he has obtained from the same species of bark.

The characteristics of this bark are very remarkable; the extreme hardness and density of the tissue distinguish it from that of all other cinchonas, and it is not surprising to find that it yields fresh alkaloids.

It was first imported in 1871, and was examined by Dr. Flückiger, and by him named, as above mentioned, *China Cuprea*. Within the last few months it has been sent over in immense quantities from Buccarramanga, in the province of Santander, where it is said to form whole forests, all other species of cinchona being found in their native forests in small clumps or isolated trees.

It varies greatly in value, some specimens yielding no quinine, while others give upwards of 2 per cent.; there is also found in most samples a small percentage of quinidine and cinchonine, but we have not yet found cinchonidine present.

The new alkaloid, which we have been for some time investigating, presents a singular analogy to quinine in its properties, and the analysis of the platinum salt points to a composition identical with or closely resembling that of quinine.

The specific rotary power also is very near that of quinine, from which it differs in the solubility of its salts, and the readiness with which it crystallises from ether. We would therefore suggest the name of Homoquinine, following the nomenclature adopted by Dr. Hesse, who has distinguished as homocinchonidine an alkaloid closely resembling cinchonidine in its general characteristics and action on polarised light, but differing slightly in the solubility and appearance of its salts.

The alkaloid which we are describing is but moderately soluble in ether, 100 c.c. of ether free from alcohol dissolving only 0.57 at 12°; it is more soluble in ether containing alcohol; when 8 per cent. of the latter is present 100 c.c. dissolves 2.27. Alcohol of 90 per cent. at 12° dissolves 7.64 per 100 c.c.

When impure and mixed with other alkaloids it is much more soluble, and it is very apt to shew supersaturation to a great extent.

The *sulphate* resembles that of quinine in appearance, but crystallises in shorter needles; it appears to contain 6 mols. of water, but effloresces so readily that the exact hydration is difficult to determine. It is but slightly soluble in water, 1 part of the salt requiring upwards of 100 parts of water at 100° for solution. On cooling the solution crystallises, leaving 0.25 per 100 c.c. in solution. A slight excess of acid greatly increases the solubility, and the bisulphate is extremely soluble, and crystallises with difficulty in long needles.

The *neutral sulphate* is scarcely soluble in strong spirit, but is somewhat more soluble in spirit of 50 per cent. than in water.

The *oxalate* is very like that of quinine, and dissolves with difficulty in boiling water, from which it crystallises on cooling.

The *tartrate* is but very slightly soluble in water, and closely resembles the tartrates of quinine and cinchonidine. The *hydrochloride* and *nitrate* are very soluble, and separate, on cooling or evaporation of a strong solution, as oily layers. The *hydriodide* closely resembles that of quinine. On cooling a hot saturated solution of the alkaloid in spirit there is a similar separation of the alkaloid as an oily substance; from less concentrated solutions it crystallises in small needle-shaped crystals.

The platinum salt contains water of crystallisation, which is lost at 140° . On incineration of the anhydrous salt it gives 26.74 per cent. Pt; the corresponding salt of quinine gives 26.73 per cent.

We have not found the alkaloid to give *Dalleiochine* with chlorine and ammonia.

The solutions of the sulphate in excess of acid are fluorescent.

The iodosulphate is more soluble than that of quinine, but does not crystallise so readily.

The alkaloid and its salts give a left-handed rotation to the polarised ray, nearly approaching that of quinine. The alkaloid in a 5 per cent. solution in spirit of 90 per cent. shows a rotation of -158° .

The sulphate in a 5 per cent. solution in water containing 0.5 per cent. H_2SO_4 shows a rotation of -209° for the anhydrous salt, with 1 per cent. of acid present in excess, of 220° . Further investigations on larger quantities of this interesting body are required to determine all its relations, but in the meantime the results given above seemed to us of sufficient importance to bring before the Society.

XIII.—Contributions to the Chemistry of Rare Earth-Metals.

By B. BRAUNER, Ph.D., Fellow of the Owens College.

WITHIN recent times the chemistry of the rare earth-metals, owing to the discovery of several new elements, has attracted the attention of many chemists. The classical researches of Berzelius, Mosander, Marignac, Bunsen, Rammelsberg, Hermann, and others have certainly furnished us with copious experimental material, and explained many points of the chemistry of the rare earth-metals. These facts, however, could not be arranged systematically, nor could the relations in which this group of elements stand to other groups be determined. So much indeed is this the case, that the rare earth-metals and their compounds have not unfrequently been regarded as holding an excep-

tional position, finding only a certain analogy in the elements of the magnesium group.

A great step forward was made by Mendelejeff in the years 1870 and 1871, for having established the periodic law in its present state (*Liebig's Annalen*, Suppl. 8, 133), he came to the conclusion that the rare earth-elements can be systematically placed, only by assuming that the hitherto accepted atomic weights are only two-thirds of the truth.

Mendelejeff's view has been confirmed by the determination of the specific heat of cerium by himself (*Bull. de l'Acad. de St. Petersbourg*, 1870, 445), by the investigations of Cleve (*Bull. Soc. Chim.* [2], 21, 203), and Nilson (*Berl. Ber.*, 8, 655; 9, 1056, 1142, 1722), and lastly by Hillebrand's (*Pogg. Ann.*, 158, 71) determinations of the specific heats of metallic lanthanum, cerium, and didymium.

The position of the individual members of the cerite metals in the periodic system has not yet been satisfactorily established, in spite of the endeavours of several authors. Thus Mendelejeff (*loc. cit.* and *Liebig's Annalen*, 168, 45) places cerium (Ce = 140) in the fourth group (vertical), but he is doubtful as to the position of lanthanum and didymium.

Lothar Meyer (*Moderne Theorien*, 3rd Edition, 293), on the other hand, places cerium (Ce = 137) in the third group, lanthanum (La = 139) in the fourth group, and didymium (Di = 147) provisionally in the sixth group; but later on he (*ibid.*, 4th Edit., 138) places all three elements (La = 139, Di = 140, Ce = 141) in the third group.

Several years ago the author of the present communication (*Berl. Ber.*, 11, 873, Note) proposed the hypothesis that the cerite metals might be placed in the 8th series (horizontal) of the periodic system as follows:—

	Group III.	IV.	V.
	La.	Ce.	Di.
Series 8	139	141.6	147

The object of the research, the chief results of which are given in the present paper, is the study of the cerite metals with special reference to their position in the periodic system. It appeared desirable to examine which one of the above-mentioned views is correct, and to collect further facts in its support.

A. Cerium Tetrafluoride.—If cerium stands in the place which was allotted to it by Mendelejeff in the periodic system, a compound of the above composition ought to exist, and though Berzelius (see *Gmelin-Kraut's Handbuch der Chemie*, II, 1, 520) may possibly have prepared a body of this kind, no analysis was made, and it therefore may have been a fluoride, an oxyfluoride, or a double fluoride. The

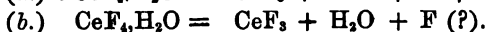
mineral "Fluocerite" is indeed generally regarded as CeF_4 , but the only published analysis by Berzelius (see *Dana's System of Mineralogy*, 126) (1818) agrees better with the formula $\text{Ce}_2\text{F}_6 + \text{H}_2\text{O}$, as the percentage of cerium is much too high to agree with CeF_4 .

By repeatedly dissolving and precipitating the basic sulphate of cerium (see Bunsen, *Pogg. Ann.*, 155, 375), and treating the hydroxide several times with chlorine in a solution of potassium hydroxide, the author prepared the pure hydrated dioxide, $\text{Ce}_2\text{O}_4 + 3\text{H}_2\text{O}$, the hydrochloric solution of which gave the spark-spectrum of pure cerium without any lines of foreign metals.

By treating the hydroxide with aqueous hydrofluoric acid, the yellow colour of the former disappeared, and after drying at 100° , a brownish powder was obtained, the analysis of which gave numbers agreeing with the formula $\text{CeF}_4 + \text{H}_2\text{O}$.

		Calculated.	Found.		
C	=	60.00	60.83	60.49	—
F	=	32.34	31.02	—	—
H ₂ O	=	7.66	—	—	7.22
		<hr/> 100.00			

Hydrated tetrafluoride of cerium is an amorphous brownish powder, insoluble in water, which on heating loses its water and a part of its fluorine as hydrofluoric acid; on heating more strongly a gas is given off, which decomposes potassium iodide with liberation of free iodine. The decomposition seems to occur according to both of the following equations:—



On heating for some time over the blowpipe, in contact with moist air, pure cerium dioxide is left behind:



Double Salt of Cerium Tetrafluoride.—The hydrated dioxide was treated with a solution of potassium-hydrogen fluoride, and a salt was obtained, the composition of which corresponded with the formula $3\text{KF} \cdot 2\text{CeF}_4 + 2\text{H}_2\text{O}$:

		Calculated.	Found.			
K	=	18.17	19.61	19.33	—	—
Ce	=	43.79	42.39	42.31	43.39	43.25
F	=	32.45	—	—	32.32	32.33
H ₂ O	=	5.59	—	—	—	—
		<hr/> 100.00				
						5.31

It is a slightly yellowish-white crystalline powder, consisting of very small microscopical octohedrons and cubes (?). It is insoluble in water, and is converted by sulphuric acid into a mixture of potassium sulphate with the orange-yellow sulphate of cerium dioxide, hydrofluoric acid being given off at the same time. On heating, it behaves similarly to the hydrated tetrafluoride.

B. *Peroxide of Didymium*.—Mosander, Marignac (*Ann. Chim. Phys.* [4], 38, 148), Hermann (*J. pr. Chem.*, 82, 385), and Zschiesche (*J. pr. Chem.*, 104, 74) observed, that didymium forms, besides the grey oxide (now D_2O_3), a higher oxide of a brown colour; but they were unable to determine its true composition, finding that the substance contained only 0.32 to 0.88, or 0.446 or 0.35 per cent. of oxygen more than the ordinary oxide. Afterwards this body was obtained in a purer state by Frerichs and Smith (*Lieb. Ann.*, 191, 331), who succeeded in converting 100 parts of D_2O_3 into 107.13 parts of the higher oxide, this corresponding to the formula D_4O_5 , which formula Lothar Meyer (*Moderne Theorien*, 3rd Edit., 322) considers as doubtful.

Some years ago the author suggested that the composition of this higher oxide, in the pure state, would be found to correspond with the formula D_4O_5 , and that didymium would find its proper position among the elements in the fifth group. Cleve (*Bihang till K. Svenska Akad. Handl.*, Bd. 2, 88) and Nilson (*Berl. Ber.*, 8, 655) regard this oxide as D_2O_3 ; Mendelejeff (*Principles of Chemistry*, 3rd Edit., 936) considers it to be either D_2O_3 or D_2O_2 .

Cleve (*Berl. Ber.*, 11, 910) repeated the preparation according to Frerichs and Smith's method, but was unable to obtain an oxide of the formula D_4O_5 , his brown oxide showing only a very small loss of 0.98 per cent. on reduction in hydrogen, so that almost all handbooks contain the statement that this oxide does not exist.

In spite of these negative experiments, the existence of such a peroxide appeared so probable, that the author deemed it necessary to attack the question again, starting from pure material.

Didymium sulphate was first purified by a long series of crystallisations, and the hot aqueous solution partially precipitated by oxalic acid. On igniting, transforming into the anhydrous sulphate, dissolving in water, reprecipitating, and repeating this process very many times, an oxide was finally obtained, the hydrochloric solution of which gave the spark-spectrum of pure didymium and an atomic weight as follows:—

Experi- ment.	Weight of Di_2O_3 .	Weighed sulphate.	Percentage in the sul- phate of		Atomic weight of didymium.
			Di_2O_3 .	SO_3 .	
I.	0·82867	1·41228	58·676	41·324	146·55
II.	0·82183	1·40050	58·681	41·319	146·58
III.	1·18879	2·02473	58·685	41·315	146·60
Mean.	—	—	58·681	43·319	146·58

The atomic weight of didymium is 146·58, if $\text{O} = 16$, $\text{S} = 32\cdot074$, or $\text{Di} = 146\cdot18$, if $\text{H} = 1$ and $\text{O} = 15\cdot96$.

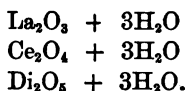
It was only after a long series of negative results that the author succeeded in preparing peroxide of didymium in the pure state. He first confirms Cleve's experiment, showing that an oxide, Di_4O_9 , cannot be prepared by Frerichs and Smith's method, 100 parts of Di_2O_3 having taken up only 1·22, 2·18, 2·77, 3·55 parts of oxygen, instead of 7·13 parts.

In the second place, Marignac and Hermann's method was tried, but without success. This consisted in heating the nitrate in the air and then treating the mixture of oxides thus obtained, either with dilute nitric acid or with a boiling solution of ammonium chloride. It is well known that no higher oxide is formed by melting the lower oxide with a mixture of potassium hydroxide and chlorate, or on treating it with hypochlorous acid. The methods finally adopted are as follows:—

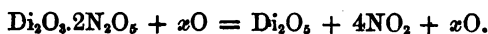
I. *Hydrated peroxide of didymium* is obtained as an amorphous greenish precipitate by the addition of dilute potash-solution to a mixture of the solutions of didymium nitrate and hydrogen dioxide, until a slightly alkaline reaction occurs. After drying this precipitate in a vacuum, a light red powder was obtained, corresponding with the formula $\text{Di}_2\text{O}_5 + 3\text{H}_2\text{O}$.

	Calculated.	Found.
Di_2O_5	79·87	78·48
O_2	7·49	8·51 (by diff.)
H_2O	12·64	13·01
	<hr/> 100·00	<hr/> 100·00

This hydrate is analogous to the hydrates of lanthanum and cerium, the amount of oxygen increasing with increasing atomic weight.



II. *Anhydrous Didymium Pentoxide*.—On carefully heating basic nitrate of didymium to dull redness, in a current of oxygen in a porcelain boat, the oxide Di_2O_3 was obtained as an amorphous chocolate-brown mass, according to the equation



It was found, as an average of many determinations, that 109 parts of the pentoxide gave 100 parts of Di_2O_3 , or in percentage:—

	Calculated.	Found.
Di_2O_3	91.42	91.37
O_2	8.58	8.63
	<hr/> 100.00	<hr/> 100.00

The specific gravity varies according to the mode of preparation. The following numbers were obtained for the specific gravity in benzene at 15°C .:—

5.171
5.261
5.262
5.358
5.651

5.368

On heating to a high temperature, oxygen is given off, as can be easily shown by applying a red-hot splint of wood to the gas contained in the crucible. The oxide may be heated in hydrogen above the boiling point of sulphur, without being reduced; the reduction begins to take place only at dull red heat, when water is deposited in the colder part of the tube.

Pentoxide of didymium dissolves in dilute nitric acid or sulphuric acid without evolution of gas, but on dissolving it in stronger acids, oxygen, containing some ozone, is given off. On treating the pentoxide with concentrated hydrochloric acid, only a small quantity of chlorine is given off, whilst hydrofluoric acid does not act upon it. It is only slightly soluble in a cold concentrated solution of ammonium nitrate. A solution of the same strength dissolves the oxides named below, in the following proportions:—

Di_2O_3 .	Di_2O_3 .	La_2O_3 .
1 part	10 parts	29 parts

This different solubility of the oxides of lanthanum and pentoxide of didymium in ammonium nitrate could not, however, be used for a quantitative separation of the above-named oxides, though it furnishes a simpler mode of preparing pure lanthanum and didymium oxides than the methods hitherto proposed. For this purpose a mixture of lanthanum and didymium nitrates, free from yttrium and cerium, is heated in a current of oxygen, to convert the didymium into the peroxide, and then treated with a cold neutral solution of ammonium nitrate, sufficient to bring half of the oxides into solution. The dissolved, as well as the undissolved, portion is treated in the same way two or three times with smaller quantities of ammonium nitrate, and in this manner very nearly pure preparations may be obtained.

III. The following experiments were made, with the view of ascertaining whether salts of didymium pentoxide can be prepared. A solution of the pentoxide in acids leaves on evaporation in a vacuum only the salts of the lower oxide. On mixing a solution of the pentoxide in sulphuric acid with one of potassium sulphate, the salt $\text{Di}_2\text{O}_3.3\text{SO}_3 + 3\text{K}_2\text{O}.5\text{SO}_3$ is thrown down:—

	Calculated.	Found.
Di_2O_3	= 30.86	30.68 —
K_2O	= 25.68	25.80 —
SO_2	= 43.46	— 43.99
	<hr/> 100.00	

From a mixture of didymium sulphate solution with hydrogen dioxide, potassium sulphate throws down the precipitate $\text{Di}_2\text{O}_3.3\text{SO}_3 + 4\text{K}_2\text{O}.5\text{SO}_3$.

	Calculated.	Found.				
Di_2O_3	= 26.68	27.75	28.16	—	—	—
K_2O	= 29.49	29.98	29.94	—	—	—
SO_3	= 43.83	—	—	43.51	43.86	44.02
	<hr/> 100.00					

Both of these salts form pink crystalline powders.

I attempted to prepare double fluorides containing didymium as DiF_3 or DiOF_3 . For this purpose a solution of acid potassium fluoride was evaporated to dryness with anhydrous didymium pentoxide, and the salt fused. The oxide lost its brown colour, and was converted into the salt $3\text{KF}.2\text{DiF}_3 + \text{H}_2\text{O}$.

		Found.				
Calculated.						
Di = 48·91	49·00	49·23	48·79	47·98	49·17
K = 19·57	19·40	18·93	—	—	—
F = 28·52	—	—	23·67	25·87	26·82
H ₂ O = 3·00	—	—	—	—	2·94
<hr/>						
100·00						

The salt forms a pink powder, insoluble in water, yielding on evaporation with sulphuric acid hydrofluoric acid and a mixture of the sulphates of didymium and potassium.

Another salt, prepared in the same way, was the following:—
 $3\text{KF} \cdot 3\text{DiF}_3 + \text{H}_2\text{O}$.

		Calculated.	Found.	
Di ₃ = 54·75		54·43	—
K = 14·61		14·67	—
F = 28·40		—	—
H ₂ O = 2·24		—	2·73
<hr/>				
100·00				

On treating the hydrated pentoxide with a cold solution of acid potassium fluoride, it was converted into a pink salt having the composition $3\text{KF} \cdot 4\text{DiF}_3 + 3\text{H}_2\text{O}$.

		Calculated.	Found.		
Di = 56·14		56·77	57·14	—
K = 11·25		11·41	10·69	—
F = 27·33		—	—	—
H ₂ O = 5·18		—	—	4·85
<hr/>					
100·00					

The three last-mentioned salts are the first double fluorides of a rare earth R_2O_3 that have been prepared.

The transformation of Di_2O_3 into Di_2O_5 , involving an increase of weight of 8·58 per cent., may be regarded as the only chemical reaction by which the purity of didymium preparations can be tested.

C. *On the Atomic Weight of Lanthanum*.—Pure lanthanum salts were prepared by heating a solution of anhydrous sulphate in six parts of water to 35°, and recrystallising six times in this way. The oxide finally obtained was treated with ammonium nitrate, and the same process was repeated several times with the part dissolved. After examining the spark and absorption spectrum of the last product, it was found to be perfectly pure lanthanum.

The atomic weight determinations gave the following numbers:—

Weight of oxide.	Sulphate.	P. c. of La_2O_3 .	Atomic weight.
1.75933	3.05707	57.566	139.94
0.92417	1.60589	57.549	139.83

Mean..... 139.88

The mean atomic weight of lanthanum is 139.88 ($\text{O} = 16$), which is the same that has been found by Marignac and Cleve. The round number 139 may therefore be considered to be the atomic weight of lanthanum.

Conclusion.

Whilst the above experiments were in progress, Nilson and Pettersson (*Berl. Ber.*, 13, 1459) published a series of objections to the periodic system, one of which consisted in the statement, that insurmountable difficulties present themselves to the classification in the system of the numerous rare earth-elements.

The results obtained in the present communication prove that with the metals cerium, lanthanum, and didymium, this is *not the case*; but that, on the contrary, each of these metals is now found to occupy its own characteristic position in the system. This is seen from the following facts:—

Cerium, with the atomic weight $\text{Ce} = 141.6$ (Bübrig) and the higher oxide CeO_3 , finds its place in the fourth group, 8th series (see the table below). It forms salts analogous to the salts of other elements belonging to the same group, e.g., the sulphates:—

$\text{TiO}_2.2\text{SO}_3$ anhydrous and $+ 3\text{H}_2\text{O}$.

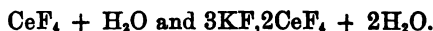
$\text{ZrO}_2.2\text{SO}_3$ anhydrous and $+ 4\text{H}_2\text{O}$.

$\text{SnO}_2.2\text{SO}_3$ anhydrous and hydrated.

$\text{CeO}_2.2\text{SO}_3 + 4\text{H}_2\text{O}$ and $7\text{H}_2\text{O}$.

$\text{ThO}_2.2\text{SO}_3$ anhydrous and $+ 3, 4, 4\frac{1}{2}, 8$, and $9\text{H}_2\text{O}$.

The position of cerium in the fourth group is further confirmed by the existence of the compounds:—



Another series of corresponding compounds is the following:—

Type RX_4	$\left\{ \begin{array}{l} \text{CO}_2 \\ \text{CCl}_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{SiO}_2 \\ \text{SiCl}_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{TiO}_2 \\ \text{TiCl}_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{ZrO}_2 \\ \text{ZrCl}_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{SnO}_2 \\ \text{SnCl}_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{CeO}_2 \\ \text{CeF}_4 \end{array} \right.$	$\left\{ \begin{array}{l} \text{PbO}_2 \\ (\text{PbCl}_4) \end{array} \right.$	$\left\{ \begin{array}{l} \text{ThO}_2 \\ \text{ThCl}_4 \end{array} \right.$
Type RX_3	$\left\{ \begin{array}{l} (\text{C}_2\text{O}_3) \\ \text{C}_2\text{Cl}_6 \end{array} \right.$	$\left\{ \begin{array}{l} — \\ \text{Si}_2\text{Cl}_6 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Ti}_2\text{O}_3 \\ \text{Ti}_2\text{Cl}_6 \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} \text{Ce}_2\text{O}_3 \\ \text{Ce}_2\text{Cl}_6 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Pb}_2\text{O}_3 \\ — \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \end{array} \right.$

Didymium, with its atomic weight $\text{Di} = 146.6$, the peroxide, Di_2O_5 , and its hydrate, $\text{Di}_2\text{O}_5 + 3\text{H}_2\text{O}$, finds its place in the fifth group, 8th series. Moreover, the elements vanadium and bismuth, belonging to

the same group, form oxides, which give the peroxide reaction. The specific volume of didymium pentoxide is = 34.8, and from this number didymium finds a position in the fifth group, 8th series, if we arrange the specific volumes of the *higher* oxides according to the periodic system (Brauner and Watts, *Phil. Mag.* [5], 11, 60).

	$\frac{1}{2}\text{V}_2\text{O}_5$	$\frac{1}{2}\text{Nb}_2\text{O}_5$	$\frac{1}{2}\text{Di}_2\text{O}_5$	$\frac{1}{2}\text{Ta}_2\text{O}_5$
Volume.....	26	30	34.8	31

The other corresponding compounds are the following, most of them being *lower* compounds:—

Type RX_5	{ N_2O_5	P_2O_5	V_2O_5	As_2O_5	Nb_2O_5	Sb_2O_5	Di_2O_5	Bi_2O_5
Type RX_3	{ N_2O_3	(P_2O_3)	V_2O_3	As_2O_3	Nb_2O_3	Sb_2O_3	Di_2O_3	Bi_2O_3
	NCl_3	PCl_3	VOCl_2	AsCl_3	NbCl_3	SbCl_3	DiCl_3	BiCl_3
	NOCl	—	VOCl	AsOCl	—	SbOCl	DiOCl	BiOCl

Lanthanum, $\text{La} = 139$, can be placed only in Group III, series 8, between barium, $\text{Ba} = 137$, and cerium, $\text{Ce} = 141.6$, as it forms only the oxide La_2O_3 . Its compounds are in like manner analogous to the compounds of the other elements belonging to the same group.

The Periodic System of Elements.

Groups :	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series :	$\overline{\text{R}_2\text{O}}$	$\overline{\text{R}_2\text{O}_2}$	$\overline{\text{R}_2\text{O}_3}$	$\overline{\text{RH}_4}$ R_2O_4	RH_3 R_2O_5	RH_2 R_2O_6	RH R_2O_7	(R_2H) (R_2O_8)
1 2	$\text{}^1\text{H}$ $\text{Li } 7$	$\overline{\text{Be } 9}$	$\overline{\text{B } 11}$	$\overline{\text{C } 12}$	$\overline{\text{N } 14}$	$\overline{\text{O } 16}$	$\overline{\text{F } 19}$	—
3 4	$\text{}^{23}\text{Na}$ $\text{K } 39$	$\text{}^{24}\text{Mg}$ $\text{Ca } 40$	$\text{}^{27}\text{Al}$ $\text{Sc } 44$	$\text{}^{28}\text{Si}$ $\text{Ti } 48$	$\text{}^{31}\text{P}$ $\text{V } 51$	$\text{}^{32}\text{S}$ $\text{Cr } 52$	$\text{}^{35.5}\text{Cl}$ $\text{Mn } 55$	$\text{Fe } 56, \text{Co } 59, \text{Ni } 59, \text{Cu } 63.$
5 6	(63 Cu) $\text{Rb } 85$	$\text{}^{65}\text{Zn}$ $\text{Sr } 87$	$\text{}^{69}\text{Ga}$ $\text{Y } 89$	$\text{}^{72}\text{P}$ $\text{Zr } 90$	$\text{}^{75}\text{As}$ $\text{Nb } 94$	$\text{}^{78}\text{Se}$ $\text{Mo } 96$	$\text{}^{80}\text{Br}$ $\text{? } 100$	$\text{Ru } 104, \text{Rh } 104, \text{Pd } 106, \text{Ag } 108.$
7 8	(108 Ag) $\text{Cs } 133$	$\text{}^{112}\text{Cd}$ $\text{Ba } 137$	$\text{}^{114}\text{In}$ $\text{La } 139$	$\text{}^{118}\text{Sn}$ $\text{Ce } 141.6$	$\text{}^{120}\text{Sb}$ $\text{Di } 146.6$	$\text{}^{126}\text{P Te}$ $\text{Tb } 148.8$	$\text{}^{127}\text{I}$ $\text{? } 150$	$\text{? } 152, \text{? } 153, \text{? } 154, \text{? } 156.$
9 10	$\text{}^{156}\text{P}$ $\text{? } 170$	$\text{}^{158}\text{P}$ $\text{? } 172$	$\text{}^{159}\text{P}$ $\text{Yb } 173$	$\text{}^{162}\text{P}$ $\text{? } 177$	$\text{}^{166}\text{Er ?}$ $\text{Ta } 182$	$\text{}^{167}\text{?}$ $\text{W } 184$	$\text{}^{169}\text{?}$ $\text{? } 190$	$\text{Os } 193, \text{Ir } 193, \text{Pt } 195, \text{Au } 107.$
11 12	(197 Au) $\text{? } 221$	$\text{}^{200}\text{Hg}$ $\text{? } 225$	$\text{}^{204}\text{Tl}$ $\text{? } 230$	$\text{}^{207}\text{Pb}$ $\text{Th } 234$	$\text{}^{210}\text{Bi}$ $\text{? } 237$	$\text{}^{214}\text{?}$ $\text{U } 240$	$\text{}^{219}\text{P}$ $\text{? } 244$	

With regard to the *better studied* of the other rare earths, it appears from the experiments of Cleve, Nilson, and Pettersson, that the same conclusion, as regards the positions in the system, may confidently be drawn. Thus, *e.g.*, ytterbium, studied by Nilson, finds its position in the third group after lanthanum, the compounds of the two exhibiting a close analogy. The same follows from the experiments of Cleve or Nilson, as regards scandium, yttrium, thorium, and beryllium, the oxide of which, BeO, is a dyad rare earth (see Brauner, *Phil. Mag.* [5], 11, 65).

Is it not natural to expect that the other rare earth-metals, which have as yet been but slightly investigated, will in like manner find in time their own positions, especially if attention be directed to the higher oxides and their corresponding compounds?

XIV.—*On the Composition of Pennant Grits in contact with and at a distance from Carbonaceous Deposits.*

By EDWARD WETHERED, F.C.S., F.G.S.

THE carboniferous rocks of the West of England, above the limestone, consist of an alternation of arenaceous and argillaceous strata with seams of coal. The arenaceous strata are of two types, namely, the Millstone grit and the Pennant grit. The argillaceous beds are known by such vague terms as "Cliff," "Duns," "Shale," &c., and it is these which in almost every case immediately follow seams of coal; and in the exceptional instances, where a grit occupies that position, the latter becomes more argillaceous in contact with the coal. In this paper, however, I shall refer only to the arenaceous rocks as represented by the "Pennant" grit variety; and it will be my endeavour to show that the argillaceous character of the rocks referred to, has originated from certain products of decomposition, given off from decomposing vegetable matter acting on the original sediment of which the rocks have been built up.

The term "Pennant" has usually been confined to a thick development of bluish rock, which, in the middle series of the Bristol coal-field, attains a thickness of something like 900 feet. It is also largely developed in the Somersetshire, South Wales, and Forest of Dean coalfields; but further than this it has not been correlated. As, however, I have already implied, the Pennant grit is not confined to the one horizon named, but occurs in deposits of a lesser thickness

throughout the coal-bearing strata. The following analyses are those of typical specimens of Pennant grit, taken from the thick development of the middle series of the Bristol coalfield, and other horizons :*—

Analyses of the Pennant Grit.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
Silica.....	88·20	87·20	83·26	89·73	72·80	89·00	84·56
Alumina	5·10	4·40	2·26	2·33	5·70	5·10	5·50
Ferric oxide†.	2·57	3·13	6·16	2·85	11·56	2·50	3·10
Lime.....	0·75	1·26	2·80	1·33	0·40	0·76	1·73
Carbonaceous matter	1·25	1·45	3·25	1·29	8·70	1·50	2·60
Carbonic acid..	0·75	2·75	1·15	1·50	0·30	1·00	1·90
Magnesia.....	0·07	—	—	—	—	—	0·04
Water.....	0·45	0·65	0·70	0·75	0·40	0·55	0·60
	100·14	100·84	99·58	99·78	99·86	100·41	100·03

Now compare the above analyses with those of argillaceous strata, taken from the Bristol and South Wales coalfields.

Analyses of Argillaceous Strata.

	Shale from a grit quarry near Bristol.	"Duns" from over the "Great Vein" coal near Bristol.	"Duns" from over the "Little Vein" coal near Bristol.	"Cliff" from over the "Nine Feet" coal near Cardiff.	"Cliff" from over the "Nine Feet" coal near Aberdare.
Silica.....	80·26	63·96	74·16	70·46	66·86
Alumina.....	8·93	13·86	12·00	16·30	11·60
Ferric oxide	2·09	1·60	5·13	1·95	8·03
Lime.....	1·00	1·43	0·90	1·05	0·90
Carbonaceous matter..	4·60	15·05	5·70	7·00	8·85
Carbonic acid.....	0·50	0·30	0·60	0·43	1·50
Magnesia.....	—	—	—	trace	0·12
Sulphur.....	—	trace	trace	trace	trace
Oxide of manganese ..	—	—	0·10	0·20	0·33
Water.....	2·35	3·05	1·40	2·15	1·40
Potash.....	—	—	—	0·20	trace
	99·73	99·25	99·99	99·74	99·59

It will be seen that, with the exception of the occasional occurrence

* Nos. 5, 6, and 7 are from other horizons.

† The iron in these analyses is estimated as ferric oxide, but ferrous oxide, carbonate of iron, and silicate are also generally present. This will apply to all the analyses throughout the paper.

of manganese, sulphur, and potash, the chief difference in the two sets of analyses is the greater proportion of alumina, implied of course by the term argillaceous, but a transition from one class of rock to the other is nevertheless suggested.

I must here repeat, that it is argillaceous rocks which almost invariably overlie seams of coal; and in the exceptional cases where an arenaceous grit occupies that position, it becomes more argillaceous in its contact with the coal. The following are instances of this statement:—

1st. The "Doxall" grit of the lower series of the Bristol coal-measures, rests upon a seam of coal of the same name, and averages about 18 feet thick; the analysis of the grit 3 inches over the coal and several feet above, gave the following:—

Analysis of the Doxall Grit away from the Coal.

	Soluble in acid.	Insoluble in acid.	Total.
Silica	0·13	84·43	84·56
Alumina.....	1·86	3·64	5·50
Ferric oxide	2·36	0·74	3·10
Lime	1·33	0·40	1·73
Carbonaceous matter	—	—	2·60
Carbonic acid	—	—	1·90
Magnesia	—	—	0·04
Water	—	—	0·60
			100·03

Analysis of the Doxall Grit close over the Coal, taken from some feet below the last specimen.

	Soluble in acid.	Insoluble in acid.	Total.
Silica	0·30	75·25	75·55
Alumina.....	2·20	6·36	8·56
Ferric oxide	5·53	—	5·53
Lime	—	—	0·70
Carbonaceous matter.....	—	—	8·05
Carbonic acid	—	—	0·33
Magnesia	—	—	trace
Oxide of manganese.....	—	—	0·26
Phosphoric anhydride.....	—	—	trace
Sulphur.....	—	—	0·74
Water	—	—	0·60
			100·32

The Doxall grit, it will be observed, has become more argillaceous in the second analysis; that is to say, nearer the coal, and also contains phosphorus, sulphur, and manganese.

A second instance will be that of a grit which lies a few feet over the "Great Vein" coal at the Eastern Collieries near Bristol, where it averages about 4 feet thick.

Analysis of the Upper Portion of the Great Vein Stone, away from the Coal.

	Soluble in acid.	Insoluble in acid.	Total.
Silica	0.20	81.10	83.30
Alumina	1.06	3.40	4.46
Ferric oxide	4.46	0.80	5.26
Lime	1.16	—	1.16
Carbonaceous matter	—	—	3.80
Carbonic acid	—	—	1.40
Magnesia	—	—	0.50
Oxide of manganese	—	—	0.36
Water	—	—	0.60
			100.84

Analysis of the Lower Portion of the Great Vein Stone, close over the Coal.

	Soluble in acid.	Insoluble in acid.	Total.
Silica	0.43	75.92	76.35
Alumina	2.45	8.77	11.20
Ferric oxide	3.90	0.65	4.55
Lime	0.60	—	0.60
Carbonaceous matter	—	—	5.65
Carbonic acid	—	—	0.50
Magnesia	—	—	0.99
Oxide of manganese	—	—	trace
Water	—	—	1.00
			100.84

As the third example, two beds of Pennant grit, from the thick development in the middle coal-measures of the Bristol coalfield, were next analysed. I selected these, as they were similar, with the exception of stratified layers of carbonaceous matter in one and not

in the other; in thickness and coarseness they were alike, and were both exposed in the same quarry.

*Analysis of the Pennant Bed containing Stratified Layers of Carbonaceous Matter.**

Silica	79.36
Alumina	7.11
Ferric oxide	3.16
Lime	1.33
Carbon	8.05
Carbonic acid.....	0.90
Oxide of manganese	0.06
Sulphur	0.08
Water	0.70
	<hr/>
	100.75

Analysis of the Pennant Bed free from Carbonaceous Matter.

Silica	83.26
Alumina	2.26
Ferric oxide	6.16
Lime	2.80
Carbonaceous matter.....	3.25
Carbonic acid.....	1.15
Magnesia.....	trace
Water	0.70
	<hr/>
	99.58

In all these last analyses, the grit has become more argillaceous when in contact with carbonaceous matter, and we find manganese, sulphur, and, in one instance, phosphorus present.

To what cause are we to assign the tendency of these rocks to become more argillaceous when in contact with carbonaceous matter? I am disposed to assign it, mainly, to carbonic acid given off from decomposing vegetable matter (which produced the coal and other carbonaceous deposits) acting on the freshly formed deposits of inorganic sediment which gave rise to the strata in question. The effect of this agent would be, to decompose all silicates in the deposit with the exception of silicate of alumina,† the bases forming soluble carbo-

* The layers of carbonaceous matter averaged about 2 inches thick, and divided the rock into beds of about the same thickness. The rock analysed was freed from the carbonaceous matter attached to it.

† For the action of carbonic acid upon rocks, see Bischof's "Chemical and Physical Geology," vol. 1, page 1. For alumina as the exception, see p. 5.

nates. Some of the alumina in the analyses is, however, not combined with silica, and it therefore seems probable that it has undergone decomposition, but even if this be so, the free alumina assumes the form of a hydrated oxide, which would not be readily removed in solution. By such a process as this the alumina would increase in proportion to the whole mass of rock acted upon by the carbonic acid, by the removal of other constituents. The deposit would therefore become more argillaceous.

As to the occurrence of manganese, sulphur, and phosphorus in the strata in contact with carbonaceous matter, I attribute this to the tendency of certain inorganic substances to replace carbonaceous matter.

XV.—*Note on Certain Photographs of the Ultra-violet Spectra of Elementary Bodies.*

W. N. HARTLEY, F.R.S.E., &c., Professor of Chemistry, Royal College of Science, Dublin.

In the year 1872, when I made a series of observations on the spectra of solutions of cobalt salts, the fatigue to the eye and the labour involved in measuring the position of obscure bands, led me to the conclusion that the spectroscope would never be made available for many of the purposes to which it might be applied, until it had been combined with a photographic camera. The experiments of some five years showed me that many improvements in Miller's apparatus (*Phil. Trans.*, 1862, 152) and method of working were necessary. It is more than three years since the method of working now employed was proposed by me, and carried out in conjunction with Professor Huntington. Although the apparatus has been freely shown to those interested in the subject, a detailed account of the instruments has only quite recently been published (*Proc. Royal Dublin Soc.*, 3, Ser. II).

It must be borne in mind that wet collodion processes and films containing silver iodide are not capable of yielding accurate reproductions of more than a very limited portion of the spectrum; neither are lenses or prisms of any kind of glass, nor diffraction gratings ruled on glass or speculum metal available for the production of spectra of rays of high refrangibility. Working with prisms and lenses of quartz or Iceland spar, Professor Huntington and myself showed that the improved processes of dry plate photography were specially applicable

to spectrum work, and we were the first to employ them for the purpose (*Phil. Trans.*, Part I, 1879). The photographs we obtained were the first ever executed with unachromatised lenses, which contained the whole of the lines of metallic spectra *completely in focus on one plate, and extending from the blue to the extreme ultra-violet rays*. The absorptive power of the atmosphere places a limit to the length of the spectra at the more refrangible end, as shown by M. Cornu.

With a prolonged exposure of gelatin plates it is possible to extend the photographs through the coloured rays to the red end of the spectrum.

The published photographs of Mr. Norman Lockyer ("Studies in Spectrum Analysis," Kegan Paul and Co., 1878, London) and of Mr. Rand Capron ("Photographed Spectra," Spon and Co., 1877, London), include only the rays lying between wave-length 4500 and 3600; even Professor Draper's fine sun spectrum extends no further than 3440.

Now these spectra include rays with wave-lengths 4500 and 2000. It will therefore readily be seen that many most interesting facts may be expected to result from facilities in investigating this almost unexplored region of rays of high refrangibility.

The considerable impulse which has been given to chemical spectroscopic investigation since the introduction of dry plates for the purpose, and of my method of focussing for all rays simultaneously, together with the improvements in the optical train, for which I am indebted to a communication kindly made to me by M. Cornu (*Compt. rend.*, 86, 104), have led me to offer to the Chemical Society a series of photographs for reproduction and publication. The extreme care which was taken in securing elements of a purity as perfect as possible for use as electrodes, I have recorded in a paper now in course of publication by the Royal Dublin Society, "The Photographed Spectra of Twenty-one Elementary Substances." Very great pains were well bestowed on focussing the entire spectrum; for so good is the definition secured, that the details discernible in the glass photographs can be properly appreciated only by examination with a two-inch objective, magnifying 45 to 56 diameters.

I have made enlargements of portions of the spectra of iron, cobalt, and nickel, which show the great number of lines characteristic of those metals and their grouping exceedingly well. The enlargement is on the scale of one foot to the inch, or twelve diameters. Some idea may be conveyed of the size of the photographs when I state that between wave-lengths 4414 and 3607 the space is $7\frac{1}{4}$ inches (182 mm.), or the general size of the spectra if enlarged in their entirety would be 5 feet in length (1.75 meters). Within the space limited by the lines with the above wave-lengths, I have easily counted 95 lines in

the enlargement, 27 of which however are air-lines, which are most abundant in this part of the spectrum. With the microscope 103 lines were seen, of which number 37 were air-lines, the total number of lines counted in the iron spectrum was more than 603. Familiar acquaintance with the spectra of various metallic elements made me consider it worth while to photograph one or two fresh series in addition to those executed for the Royal Dublin Society, placing certain well-defined groups of metals together and comparing their spectra, in order to see whether the groupings of certain lines are referable to Mendelejeff's law. Photographs of the following series have been taken :—

Lithium,	Magnesium,	Aluminium,
Sodium,	Zinc,	Indium,
Potassium,	Cadmium,	Thallium,
Copper,	Carbon,	Arsenic,
Silver,	Tin,	Antimony,
Mercury,	Lead,	Bismuth.
Iron,	Palladium,	
Cobalt,	Gold,	
Nickel.	Platinum.	

The instrument used for the series to which I here make special allusion, was one furnished with short focussed lenses of large diameter. The spectra have only half the dispersion of the former series, but by the use of a somewhat different sensitive film, by reducing the exposure, and modifying the development, the greater part of the air-spectrum has so little density, that it can scarcely be printed. This gives greater prominence to the metallic lines, and brings out their peculiarities in a striking manner. Thus the density which corresponds to intensity of chemical action, the length, breadth, and shape of the lines, and the occurrence of lines in pairs, triplets, and groups, are all characteristics of importance which are more easily seen by reason of the comparative absence of air-lines.

The most striking resemblance between the spectra of any three elements, is that shown by Nos. 17, 18, 19, and 20, representing iron; nickel, cobalt, and palladium, there being the greatest similarity in appearance between iron and cobalt. The group of continuous or long lines of a sharp clean cut appearance at the less refrangible end of the spectrum in each metal is remarkable. This grouping occurs with rays of increased refrangibility in the case of cobalt, still more so with nickel. The group of rays more refrangible than Cd 17 are most numerous in the case of iron, in cobalt next, and least so in

nickel, at the same time in the same order the refrangibility and the dispersion of the rays increases. The total number of lines, including about 66 air-lines, which have been counted under the microscope, are for iron 603, for cobalt 556, and nickel 391. The apparent connection between the lines of iron and those of aluminium is not due to a similarity in the spectra of the two elements, but to a group of the iron lines making their appearance in the aluminium spectrum. There are not more than 18 lines which can be attributed with certainty to this latter element. On the other hand palladium, an element which is associated to some extent with iron, although it belongs to another group, has more the character of the iron group in its spectrum than that of any other group of elements; 399 lines have been counted in its spectrum. This does not appear to be caused by the impurity of the metal, though there will be doubt concerning this point until enlargements of the spectra have been placed side by side.

In the series magnesium, zinc, and cadmium, there is a similarity in the number, shape, and intensity of the lines. The refrangibility of the strong lines increases with the atomic weight of the elements. The fourth group of strong lines in magnesium consists of a pair of long lines with a somewhat feeble one beside them. This grouping is repeated in zinc, in which it forms the first group; in this case the lines are wider apart and of less refrangibility; the grouping is then repeated in the zinc spectrum at a point just under the strongest lines of magnesium.* A similar grouping occurs in the cadmium spectrum, consisting of the first three strong lines; in this case the lines are less refrangible and more widely separated.

There is a great similarity between the copper and silver spectra, consisting of a pair of fine but strong lines, and a scattered group of more refrangible short lines, which are rather less refrangible, but stronger in the case of silver than in that of copper. More nearly allied to these than to any other spectra, are gold and platinum.

There are three finely cut fairly strong lines in the gold spectrum, together with a more refrangible and scattered group of short lines.

There is a considerable similarity between the groups tin and lead and arsenic, antimony and bismuth.

These spectra may be described as consisting of pairs or groups of long lines not confined to a particular part of the spectrum, with interspersed dots. Arsenic, antimony, and bismuth are distinguishable by their well-marked nebulous short lines and dots, and the defined continuous edge caused by the vapour at the points of electrodes emitting a continuous spectrum. This is less observable in the spectrum of bismuth, and most so in the case of arsenic. This appearance is like-

* The extreme rays of zinc seen in the original photographs do not print, neither are the most extreme rays of aluminium visible.

wise seen in the spectrum of tellurium, and seems therefore characteristic of metalloids.

The similar character of the spectra of elements of the same series, and also a similarity in character of analogous elements of different series or elements which by their chemical properties are somewhat allied, is apparent from these photographs. Whether there are numerical relations between the wave-lengths of different groups of lines, it will be hopeless to attempt to determine, until the spectra have been reproduced on an enlarged scale, and the wave-lengths for the principal lines of the different elements calculated.

It is evident that by manipulating so as to secure omission of the air spectrum, the ultra-violet region which in any case is remarkably free from air-lines, contains the most characteristic lines and groupings of lines to be seen in the spectra of metals and metalloids.

The spectra of the alkali metals, lithium, sodium, and potassium, were obtained from electrodes by means of a condensed spark. Bullets of the metals were freed as far as possible from naphtha by cleansing with blotting-paper, and flat electrodes were then cut out of the centres of the pieces of metal. The spectra are very simple, consisting in lithium altogether of 13 lines, 11 of which are long and fairly strong lines, including the ray in the blue, while a pair of the most refrangible strong lines are accompanied by a pair of feeble duplicates. The rays are altogether more feeble than those of magnesium, cadmium, &c.

In sodium there are 24 lines, of which only 5 are long lines.

In potassium there are 47 lines, of which only 3 are long lines.

The lines are all of comparatively large wave-lengths, greater than 2800.

The increase of short lines and great increase in the proportion of short to long lines, is noticeable in those elements with the larger atomic weights.

In the magnesium and aluminium series the metals with the lowest atomic weights possess few lines arranged in well-defined groups, as in the case of magnesium, where groups of triplets appear between wave-lengths 3870 and 3900, between 3325 and 3350, between 3125 and 3100, between 2950 and 2900, at 2800 a group of four, and at 2775 a group of five exceedingly distinct lines.

Messrs. Liveing and Dewar* and M. Cornu† have described the more refrangible portions of the magnesium spectrum containing the lines above mentioned. The reversals of lines mentioned by them are not to be seen in my photographs, except in the case of the first and

* *Chemical News*, 43, 261; *Proc. Roy. Soc.*, 1881.

† *Archives des Sciences Physiques et Naturelles de Genève* [3], 2, 119—126. Cornu, *Determinations des longueurs d'onde*, &c.

third lines in the quadruple group. These two lines appear in the spectrum of the arc, but the other two do not, according to Messrs. Liveing and Dewar. Although a Leyden-jar is used with the coil, the tension of the spark which I prefer for the production of photographs is not excessive, hence doubtless the absence of reversed lines in most cases.

It may, however, here be remarked that any strong line may be reversed by over-exposing the sensitive plate, but with proper manipulation this would be unlikely to happen.

The dots are an important feature in the spectra of aluminium, indium, and thallium, and the arrangement in pairs both of the lines and of the dots is noticeable.

Notwithstanding that these substances have points in common, the spectra of these two latter elements in the general character of their lines resemble to a greater degree the spectra of the alkali metals than those of any other substances, that is to say, the characteristic appearance of their long lines is similar.

Photographs taken from the same electrode with the same spark apparatus, but executed with instruments of different dispersive powers, have in one case shown reversals of some of the longest lines in the indium and thallium spectra, but nothing of the kind is to be seen in other photographs which were executed with every perfection of manipulation. I am not prepared to say whether the greater dispersion caused the reversals to be less easily seen under the microscope, but I can confidently state that the spark apparatus worked equally well on each occasion, and therefore variations in the intensity of the spark can scarcely be the cause. That the appearance of reversed lines was not caused by over-exposure may be relied on, for indeed the appearance was that of the thinning out of the centre of the lines, and was continued to a point where, from the little density in the lines, over-exposure could not possibly have occurred. Both series of photographs are equally well in focus.

Some enlargements, measuring 36×28 inches, which have been executed for me, will serve to further the investigation of these spectra with ease and precision. The enlargements will ultimately be published by the Autotype Company, 531, Oxford Street, London.

REFERENCE TO PHOTOGRAPHS.

The spectra have been reproduced by the Woodbury Type Printing Company, Great Portland Street, London.

PLATE I.

1. Magnesium. The most refrangible line is easily resolved by a lens into a group of five fine equidistant lines.

2. Zinc.

3. Cadmium. The lines of this element have been carefully measured by M. Cornu and by M. Mascart; they have therefore been photographed at the top of Plates II and III in order to indicate the position of other metallic lines. Those lines which appear common to most of the spectra are air-lines.

4. Aluminium.

5. Indium.

6. Thallium.

7. Copper.

8. Silver.

9. Mercury.

PLATE II.

10. Graphite.

11. Tin.

12. Lead.

13. Tellurium.

14. Arsenic.

15. Antimony.

16. Bismuth.

PLATE III.

17. Iron.

18. Nickel.

19. Cobalt.

20. Palladium.

21. Gold.

22. Platinum.

XVI.—*The Chemistry of Bast Fibres.*

By C. F. CROSS and E. J. BEVAN.

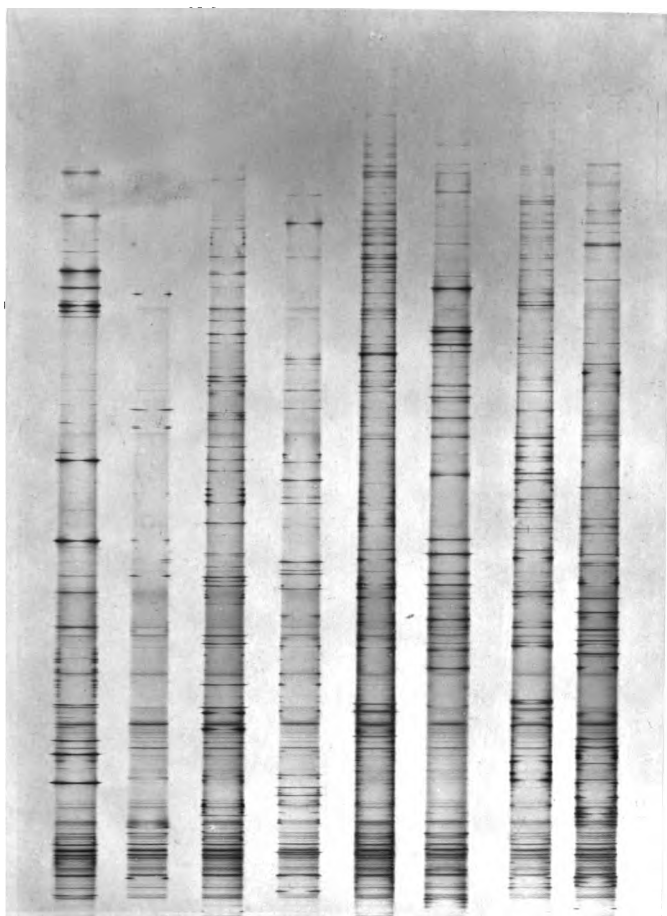
At the time of publication of the first account of our researches on this subject,* we had established the following points:—

(a.) The chemical similarity between the “non-cellulose” constituents of monocotyledonous and dicotyledonous fibres. (b.) The resolution of the jute fibre by the action of chlorine, into cellulose† on the one hand, and an aromatic body on the other, which was isolated

* Paper read before Owen's Coll. Chem. Soc., April, 1880; *Chem. Soc. J.*, 38, 666.

† In respect to the term cellulose we would observe that we attach to it only a general significance, analogous, *e.g.*, to that of the term alcohol. It is probable, as has been held by certain chemists, and confirmed by our observations, that there are numerous celluloses standing probably in both polymeric and isomeric relations to one another, and that jute cellulose may be a mixture of these. We apply the term to the aggregate isolated by any particular method, which gives the reactions generally accepted as those of pure cellulose.

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in the form of the chloro-derivative, $n(C_{19}H_{18}Cl_4O_9)$, a similar derivative being obtained from all the bast fibres (flax, hemp, manilla, &c.) examined by us, and likewise from esparto. (c.) A sufficient resemblance of the reactions of these derivatives to tetrachlorquinone to lead to the hypothesis of their being complicated derivatives of this body. (d.) The resolution of the jute fibre by boiling with dilute hydrochloric and sulphuric acids into a soluble carbohydrate, and an insoluble compound of the aromatic body, in the form of a condensed modification, with the more stable form of the cellulose. (e.) The action of dilute nitric acid on the other hand, in resolving the fibre into cellulose and a nitro-derivative of the aromatic constituents, which we investigated by way of the similar product of nitration of the esparto constituents, and found to possess the formula $nC_{25}H_{31}(NO_2)O_{23}H_8$, eight of the hydrogen-atoms being replaceable by metals. (f.) The absence of any constituent of the nature of pectose, which we established by the study of the action of boiling dilute alkalis (see page 99). (g.) By inference from these facts, under the guidance of analogy, we had further established the hypothesis that the jute fibre consists of cellulose intimately associated with a complicated body allied to the quinones, that it is in fact a "cellulide" constituted after the type of the glucosides, the aromatic body being united in this case to a cellulose in place of glucose.

In addition to these main features, the following points were incidentally observed:—

(h.) The brilliant colour-reactions of the chlorinated derivatives when freshly prepared, and their application to the detection of bast or bast constituents. (i.) The homogeneity of the jute fibre as regards the relative distribution of cellulose and aromatic bodies, and on the other hand the non-homogeneity of the cellulose isolated from the fibre by the usual methods. (k.) The advantage of substituting for the estimation of cellulose, in place of Müller's method, that of chlorination and removal of the chlorinated bodies by solution in alkalis; and (l) the increase of yield which follows from the further modification of exposing the chlorinated fibre to the action of sulphurous acid previously to the alkaline treatment.

This general view of the chemistry of bast fibres has been substantiated by our subsequent work, and in the solution of the more important special problems which it involves we have made sufficient progress to be able to lay before the Society a fairly adequate account of this branch of plant chemistry.

To the aromatic constituent of the jute fibre we may assign the formula $n(C_{19}H_{22}O_9)$. The resemblance of this to that of catechin,



is so close, that a comparative investigation of the suggested relationship to this body was necessary. Catechu was treated in the usual way for the separation and isolation of catechin and catechutannic acid. The crude products were severally treated with HCl and KClO₃ until the action was complete, and the chlorinated derivatives were isolated by the usual process of purification, *i.e.*, alternate solution in alcohol and precipitation with water, finally dissolving in absolute alcohol, filtering, and distilling off the alcohol. The analysis of these bodies gave the following results: (α) catechin derivative; (β) catechutannic acid derivative.

(α .) 0.2570 gram	yielded 0.2350 gram	AgCl and 0.0132 gram	Ag.
(β .) 0.3240	" 0.2980	" AgCl "	0.0107 " Ag.
(α .) 0.3010	" 0.4420	" CO ₂ "	0.0860 " H ₂ O.
(β .) 0.3000	" 0.4375	" CO ₂ "	0.0845 " H ₂ O.
	(α .)	(β .)	Calc. C ₂₀ H ₁₀ Cl ₄ O ₁₂ .
Cl	24.3	23.8	23.8
C	40.0	39.8	40.2
H	3.2	3.1	3.1

The products were therefore identical, and their resemblance to the before-mentioned derivatives was unmistakeable. In addition, the freshly prepared bodies gave a brilliant magenta reaction with sodium sulphite.

In the light of these results we examined a specimen of jute, rotted by shipment in the damp state, which fortunately came to hand at the moment. The aqueous extract was brown, astringent to the taste, and, at the same time, strongly acid to test-paper. It was concentrated by evaporation, digested with barium carbonate, and filtered. To the filtrate an equal bulk of strong alcohol was added, by which a flocculent precipitate was formed: this was purified by fractional precipitation with alcohol, washed with alcohol and dried, first over sulphuric acid, lastly in the air-bath at 105°. The analysis of this salt gave the following results:—

0.3735 gram gave 0.1582 gram BaSO₄.
 0.4095 " 0.4280 " CO₂, 0.1477 BaCO₃, and 0.1430 H₂O.

		Calc. C ₂₀ H ₁₀ O ₂₀ Ba ₂ .
C	30.6	30.8
H	3.9	3.7
Ba.....	24.9	24.3

It was quite insoluble in boiling alcohol, and gave no reaction with chlorine and sodium sulphite. On boiling for some time with water, it dissolved, partly separating on cooling in a gelatinous form. The

solution of the salt was accompanied by change, the gelatinous body, i.e., the free acid, having no action on alkaline copper solution, whereas the portion remaining dissolved exerted a reducing action. Analysis of the latter showed it to be similar to the above, but somewhat richer in oxygen. The ratio of carbon to oxygen is that which is characteristic of the pectic group. These facts are sufficient to establish the identity of the acid.

Determinations of cellulose in specimens of the rotted fibre yielded the following percentages: 57, 58.5, 64, 66, showing that the cellulose-yielding constituent has been degraded with formation of the soluble bodies in question.

The alcoholic filtrate from the original precipitate was evaporated to dryness, and the residue exhausted with strong alcohol. From the solution, filtered and evaporated, a substance was obtained whose aqueous solution gave the following reactions: a dark brownish-green precipitate with ferric chloride; an orange-coloured flocculent precipitate with bromine-water; the characteristic magenta reaction with chlorine and sodium sulphite; a copious precipitate with gelatin;—it was moreover strongly astringent to the taste and mordanted cotton, i.e., imparted the property of dyeing fast colours with aniline dyes. The substance dried at 105° was analysed with the following results:—

0.2040 gram gave 0.3831 CO₂ and 0.1045 H₂O.

		Calc. C ₂₆ H ₃₄ O ₁₆ .
C	51.7	51.8
H	5.7	5.6

This body is therefore proved to be a member of the tannin group. In indirect confirmation of this conclusion, we fused a quantity of the esparto resin previously described (*Chemistry of Bast Fibres*, p. 22) with potash, and isolated the products in the usual way. Phloroglucol was obtained in sufficient quantity for qualitative identification only; on the other hand, a considerable quantity of protocatechuic acid was formed. The recrystallised product was analysed with the following result:—

0.1580 gram gave 0.3150 gram CO₂ and 0.0525 H₂O.

		Calc. C ₇ H ₆ O ₄ .
C	54.4	54.5
H	3.7	3.8

The reactions and melting point were moreover those of pure protocatechuic acid.

The general identity of these non-cellulose constituents with the class of astringent substances, or tannins, is thus fully established.

In what relationship they stand to the prototype, gallo-tannin or digallic acid, is a problem which remains to be solved for them as for the entire group. All that can be said with certainty, is that the molecule of these bodies is extremely large. Their existence in plants in the closest union with cellulose, we shall discuss hereafter.

In connection with the foregoing, we have to describe certain observations on the halogen-derivatives of these bodies, additional to those previously discussed.

Determinations have been made of the yield of the chlorinated product ($C_{22}H_{22}Cl_4O_{10}$) of the action of $KClO_3$ and HCl upon pure esparto resin. Previously to the determinations, the specimen was dissolved in hot glacial acetic acid; the portion (β) which separated out on cooling was collected separately, redissolved, and precipitated with water, then washed and dried. The portion (α) remaining dissolved in the acetic acid was also precipitated with water, washed, and dried.

(α .)	{	0.5000	yielded	0.3350	gram	Cl compound.
		0.5000	"	0.3380	"	"
(β .)		0.5000	"	0.3370	"	"

The percentage yielded in the three cases is uniformly 67.

The crude esparto resin, *i.e.*, as precipitated from the alkaline liquors of the paper-maker and washed with cold water, gives up a certain quantity of substance to boiling water. The first extract, in one experiment, gave with bromine-water an orange-coloured precipitate of a highly brominated body, $n(C_{17}H_{14}Br_4O_6)$ (α); the third extract gave a similar product, $n(C_{16}H_{12}Br_4O_6)$ (β).

The analysis of these bodies is appended.

(α .)	0.6855	gram	gave	0.8085	AgBr	and	0.0032	Ag.
	0.2487	"	"	0.2905	CO ₂	"	0.0475	H ₂ O.

		Calc. $C_{17}H_{14}Br_4O_6$.
C 31.8	32.1
H 2.1	2.2
Br 50.5	50.4

(β .)	0.3185	gram	gave	0.3995	AgBr	and	0.0032	Ag.
	0.1225	"	"	0.1370	CO ₂	"	0.0235	H ₂ O.

		Calc. $C_{16}H_{12}Br_4O_6$.
C 30.5	30.4
H 2.1	2.0
Br 54.1	54.0

A second portion of this third extract was evaporated to a small bulk; and the brown plastic substance which separated was dissolved

in alkali and precipitated as a chlorinated body, by a stream of chlorine gas (α). The residue from the repeated extraction was treated with KClO_3 and HCl (β). Both products were dissolved in glacial acetic acid and filtered, and the solution was poured into a large quantity of a clear solution of bleaching powder: the precipitates collected, purified, and analysed after drying at 100° .

(α .)	0.4365 gram	gave 0.4085 AgCl and 0.0080 Ag.	
	0.2300	„ „	0.0795 H_2O „ 0.3830 CO_2 .
(β .)	0.5745	„ „	0.5665 AgCl „ 0.0045 Ag.
	0.2470	„ „	0.0995 H_2O „ 0.4090 CO_2 .

			Calc. $\text{C}_{27}\text{H}_{23}\text{Cl}_4\text{O}_{10}$.
C	45.4	45.1	44.7
H	3.8	4.4	3.9
Cl	23.8	24.6	24.1

These products are therefore identical with one another and with the derivative described in our original paper. The results are interesting for their uniformity, as showing that constant results are obtainable, at least in what are end-products, even although the physical properties of the substances dealt with are difficult of definition.

From the aromatic constituent of the esparto fibre, two other halogen-derivatives have been prepared as follows:—*Bromine compound*: by heating the purified resin in acetic acid solution with bromine, precipitating with water, redissolving in acetic acid, and heating again with bromine, precipitating, and purifying in the usual way. *Chlorine compound*: by heating esparto, cut into small pieces, with chlorine gas; extracting with alcohol and purifying as in previous cases. The analyses gave the following results:—

0.3115 gram	gave 0.2755 AgBr and 0.0047 Ag.	
0.2350	„ „	0.3335 CO_2 „ 0.0735 H_2O .
0.1910	„ „	0.2750 CO_2 „ 0.0565 H_2O .

			Calc. $\text{C}_{27}\text{H}_{23}\text{Br}_4\text{O}_{10}$.
C	38.7	39.2	38.9
H	3.5	3.3	3.4
Br	38.7	—	38.4

Chlorine compound:—

0.3055 gram	gave 0.2480 AgCl and 0.0090 Ag.	
0.2515	„ „	0.4335 CO_2 „ 0.1220 H_2O .
0.1650	„ „	0.2825 CO_2 „ 0.0715 H_2O .

			Calc. $C_{27}H_{22}Cl_4O_{12}$.
C	47.0	46.7	46.8
H	5.4	4.8	4.8
Cl	21.0		20.6

The action of chlorine on the jute fibre has been discussed at length in our original paper. We have since investigated the action of caustic alkalis upon the resulting derivative, $C_{19}H_{18}Cl_4O_8$. A specimen of the pure preparation was dissolved in a warm solution of potassium hydrate, the solution acidified with hydrochloric acid, and the resulting precipitate collected, washed, and dried. It was purified by solution in absolute alcohol and precipitation with water: it was lastly dried at 105° and analysed, with the following results:—

0.3620 gram gave	0.2310 AgCl	and	0.0077 Ag.
0.2940 " "	0.1750 AgCl	"	0.0190 Ag.
0.2920 " "	0.5345 CO_2	"	0.1300 H_2O .
0.2445 " "	0.4410 CO_2	"	0.0990 H_2O .

			Calc. $C_{18}H_{20}Cl_2O_8$.
C	49.9	49.2	49.6
H	4.9	4.5	4.6
Cl	16.5	16.8	16.3

By the action of potash, therefore, two of the chlorine-atoms have been removed, as in the case of chloranil. The further slight incidental changes in composition which prevent our representing the reaction by the symmetrical equation of saponification, are characteristic of these complex amorphous bodies.

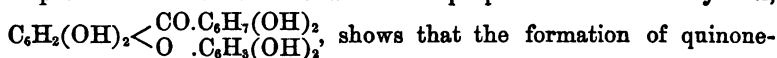
The action of bromine on the jute fibre we had investigated only as a method (Müller's) of preparing pure cellulose, and we found that it was characterised by the formation of brominated derivatives of the aromatic constituents; but it was impossible to isolate them in any quantity. A portion of the fibre was therefore treated with dilute nitric acid (5 per cent.) at 60° , washed, and exhausted with caustic soda solution. The solution was acidified with hydrochloric acid, the precipitate collected, washed, and dissolved in alcohol. Bromine was then added, and the solution allowed to stand some time. On adding water, a flocculent precipitate of the brominated derivative was obtained; this was purified in the usual way and then analysed.

{ 0.2880 gram gave	0.1555 AgBr	and	0.0052 Ag.
{ 0.2780 " "	0.1500 AgBr	"	0.0032 Ag.
0.2465 " "	0.4210 CO_2	"	0.0940 H_2O .

			Calc. $C_{26}H_{22}Br_2O_{11}$.
C	46.6		46.2
H	4.2		4.1
Br (mean of 2) ..	23.9		23.7

The similarity of this to the derivatives of the esparto constituent is noteworthy: that only two atoms of bromine have been introduced is due to the fact that the action took place in the cold.

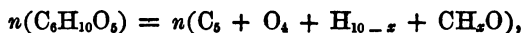
In regard to the actual constitution of these derivatives we have no very direct evidence: all our efforts to resolve them proximately into bodies of known constitution have hitherto failed. The action of nitric acid, though interesting, is too destructive to throw light on the problem: the chlorinated compounds yield chloropicrin in some quantity, and an amorphous nitro-body resembling that described in our original paper. The colour-reactions of many of them are remarkably pure, and, as we have often observed, so closely similar to those of chloranil, that, taken in conjunction with the fact that they contain 4 atoms of the halogen, the conclusion is almost inevitable that the molecule is built up around this body as a centre. Nor is this supposition without other foundation (see also p. 109) (*f*). An inspection of the constitutional formula proposed for catechin by Etti,



derivatives by the chlorination of these astringent bodies is, *à priori*, most probable. If chloranil is boiled with sugar or even cellulose and water, it dissolves to a violet liquid; this solution is astringent to the taste, gives a copious precipitate with gelatin, and a dark brownish-green precipitate with ferric chloride. Moreover, on evaporation, it deposits a brown substance, which, after solution in ammonia, is precipitated by bromine-water as orange-coloured flocks of a compound exactly resembling those before described. If the action of the chloranil upon the sugar takes place in sealed tubes at 100°, there is a considerable yield of this brown substance, which behaves with alkalis and chlorine exactly like the aromatic substances obtained from bast fibres. The complexity of these bodies, which is certainly greater than that indicated by the proportional formula given above, and the absence of any strongly marked physical characteristics, are the difficulties which impede our progress.

We have now to consider the wider problem of the relation of the cellulose to the non-cellulose constituents of bast fibres, and the relation of both to the life of the plant. In these points, as might have been expected, we have been to a certain extent anticipated by the investigations and inferences of physiological botanists, notably in respect of the origin of the tannins. On this occasion we do not think it expedient to enter into an exhaustive discussion of this aspect of the subject, but must content ourselves with giving a brief account of the current theories of the biologists, for which we have referred to the works of Sachs (*Handb. der Exper. Phys. der Pflanze* [1865]) and Sachsse (*Farbstoffe, Kohlehydrate und Proteinsubstanzen* [1877]).

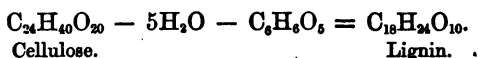
According to these observers, cellulose is directly derived from starch, or from its physiological equivalents, sugar, fat, or inulin, and is not a product of resolution of a proteid molecule. This conversion of starch into cellulose is always accompanied by the evolution of carbonic anhydride (Sachse, p. 113), and the interdependence of these phenomena has been clearly demonstrated by the researches of Sachse on the germination of *Pisum sativum*. The chemical changes attending this transformation are expressed by the following statistical equation (Sachse),



or more explicitly as a result of the observations that $\frac{2}{3}$ ths of the carbon of the starch underwent complete combustion :



The molecule, $n\text{C}_6\text{H}_{12}\text{O}_6$, is then further transformed, probably by dehydration, into substances having the atomic ratio $\text{C}_6\text{H}_{10}\text{O}_5$. By these researches it is also shown that the growth of the plant, *i.e.*, the formation of cellular tissue, and its respiration, are parallel phenomena. As regards the relation of these transformations to the chlorophyll of the plant, and those functions with which it is more especially associated, the explanation here given is entirely in harmony with the observations that, in the majority of cases, the formation of cellulose occurs in those portions from which chlorophyll is absent, whereas the formation of the parent substance, starch, is associated with the presence of chlorophyll and the evolution of oxygen. The lignification of fibres originally consisting of pure cellulose, is held by Sachs (*ibid.*, p. 369) to consist of a modification of the cell-substance (cellulose) itself, and not of infiltration of substances from the contents of the cell. The chemistry of such metamorphoses is indicated by a comparison of the composition of lignin ($\text{C}_{18}\text{H}_{24}\text{O}_{10}$) with that of cellulose ($\text{C}_{18}\text{H}_{30}\text{O}_{16}$), showing that there must occur, in addition to dehydration ($3\text{H}_2\text{O}$), a loss of oxygen (O_2). This latter probably takes the form of a more highly oxidised carbon-compound, the resolution being expressed by the following equation (Sachse) :—



Sachse is of opinion that it is to this more highly oxidised molecule that the origin of the tannins may be referred; this conclusion, however, is scarcely warranted by the equations, and as we shall presently show a much more probable mode of formation of these bodies, it must give way before a more consistent hypothesis. This is afforded by the observation of the presence in plant-structures of the pectic

group of compounds, the composition of which is much more in harmony with the equation given.* In our first paper we drew attention to a paper of Kolb's (*Bull. Soc. Ind. Mulh.*, June, 1868, and *Ann. Chim. Phys.* [4], 14, 348) on the linen fibre, in which he established the presence of a substance (about 20 per cent.) in the fibre, removable by alkalis in the form of pectic acid. On further examining his statements we find that the fibre used by him was a specimen of raw Russian flax, having the following aggregate composition (CH):—

C 43.7

H 5.9

It is obvious from these numbers that this particular fibre represented a different class from that to which jute belongs, viz., one in which the development has taken the course of converting the cellulose into bodies of lower carbon percentage. It is therefore easy to see that the results of Kolb's researches on the one hand, and our different experience with jute bast on the other are reconcilable, both with one another, and with the hypothesis given above, which is thereby strengthened.

We may here mention that that portion of the fibre known as jute "cuttings," that is to say, the root ends, containing a considerable proportion of bark, yields pectic acid when treated under pressure with a dilute solution of sodium sulphite. It is probable therefore that in the development of the jute fibre, pectous substances are likewise formed, but are transferred from the bast to the other portions of the plant.

In respect of the origin of the astringent bodies, so widely distributed throughout plant-structures, Sachs maintains, on physiological grounds, that they are degradation-products, probably of cellulose, which when formed take no further part in the metabolism of the plant, but, like urea in the animal body, are to be regarded as excreta.

If now the celluloses and the tannins are extreme terms of developmental series, it devolves upon the chemist to throw light upon the intermediate stages of the transformation, and so complete the demonstration of the biologists.

The chemical composition of the jute fibre contributes very much to the elucidation of this point, and therefore of the whole problem. The action of chlorine has been already described as effecting the resolution of the fibre into extreme products: the study of the intermediate terms of the natural series, as well as the condition of existence of the fibre substance, must be approached through the action of less drastic reagents; of these dilute sulphuric acid (5 per

* Metapectic acid is represented by the formula $C_6H_{14}O_6$.

cent.) at 80—90° C. is the most important. We have already described the soluble product of resolution of the fibre by this reagent, as a neutral body, soluble in alcohol, and, according to analysis, a carbohydrate. We have since prepared and analysed a further quantity of this substance (or mixture of substances) with the following result:—

(α .) Dried at 90°—

0.2805 gram gave 0.4575 CO₂ and 0.1580 H₂O.

		Calc. C ₁₂ H ₂₀ O ₁₀ .
C	44.4	44.4
H	6.2	6.2

(β .) Dried at 105°—

0.2460 gram gave 0.4220 CO₂ and 0.1350 H₂O.

		Calc. C ₁₂ H ₁₈ O ₉ .
C	46.8	47.0
H	6.1	5.9

(It will be observed that the aggregate composition of this substance differs but little from that of the jute itself.) The ratio H₂ : O is maintained; the substance also evinces the strong tendency to dehydration (condensation) which is characteristic of bodies of this class. Observations showed that it was not susceptible of alcoholic fermentation, and was without action on polarised light. On boiling this substance with dilute sulphuric acid in a retort it was resolved into acetic acid and furfural, which distilled, the yield of the latter being considerable, and a residue, which separated in the insoluble form, of substances yielding characteristic chlorination-products. We then made observations upon sugar, and found that when it was treated with strong sulphuric acid, and afterwards diluted and distilled, we obtained precisely the same products of resolution, confirming the conclusion therefore that a carbohydrate was present in the soluble modification of the jute fibre.

Reverting now to the action of the dilute acid upon the normal fibre, it is remarkable that the formation of the soluble modification occurs at so low a temperature as 80—90°. Moreover we found that, by successive digestions with the acid at temperatures below 100°, the greater portion of the fibre could be dissolved away in the form of this compound, and that when nine-tenths of its substance had been so removed, exposure to chlorine still caused the characteristic resolution into cellulose and chlorinated aromatic bodies. As regards the structural changes which accompany this modification, it is remarkable that the union of the fibrils into bundles remains unresolved, the appearance being that figured in our original paper (Fig. *d*). On examining this disintegrated fibre, we found that it yielded on analysis

the same percentage of cellulose as the normal fibre; thus from three specimens we isolated severally 74.4, 76.3, and 78 per cent. This result is remarkable, and is confirmed by the following additional observations:—

Four specimens of the same fibre were exposed to the action of 10 per cent. sulphuric acid at 95°. The loss sustained after 16 hours' treatment was 27.7, 28, 26.4, and 26.6 per cent. respectively. Determinations of cellulose in two of the specimens thus modified gave the numbers 75.2 and 74.7 per cent. On combustion the modified fibre was found to contain 48.1 per cent. C and 5.9 per cent. H. Not only therefore was the yield of cellulose unchanged from that of the normal fibre, but the jute had undergone no alteration in respect of its aggregate composition. Putting all these facts together—(1) the resolution of the fibre at so low a temperature as 80–90° C. by a dilute acid, *i.e.*, under conditions which are practically without influence on cellulose; (2) the identity as regards aggregate composition, (CH), of the dissolved and undissolved portions both with one another and with the original fibre; (3) the unchanged yield of cellulose; (4) the absence of perceptible variation in composition of the fibre throughout its entire length,* and (5) the absence of disintegrating action on the bundles of fibrils—we are led to the conclusion that the jute fibre is composed for the most part, *not* of cellulose, but of a transition form of cellulose from that of the original carbohydrate to its ultimate modification of a soluble astringent. It is impossible to say, supposing this transformation to be accomplished through an infinite series of terms, how many of such terms may be represented in the fibre; it is possible that cellulose is present as such, a small quantity of a soluble astringent is always found in the normal fibre; and hence it is not unlikely that the entire series may be represented. The most rational view of the jute fibre is therefore, perhaps, that it is an average aggregate of the intermediate terms of this developmental series.

The uniform disposition of the fibre constituents is shown by the following determinations of the aggregate composition and yield of cellulose from different portions of the fibre.

Aggregate composition—

(α .) Extreme upper ends. (β .) Extreme root ends.†

	(α .)	(β .)
C	47.7	47.1
H	5.9	5.7

* Negatives the hypothesis of the constitution of the fibre out of a mixture of cellulose and "encrusting" substances. See also next page.

† The extreme lower portions of commercial jute, representing a distance of about 18 inches from the actual root.

Cellulose isolated from—

(a.)
80.6 per cent.(β.)
79.9 per cent.

This uniformity of composition is visibly demonstrated, as we observed in our original paper, by treating entire lengths of the fibre (84 in.) with solutions of the aniline dyes, or of aniline sulphate. In either case a perfectly even distribution of the colour is observed, a fact which has very important technological* bearings; for as in the preparation of the fibre for spinning, very little of the averaging is resorted to, to which so much importance is attached in the manufacture of silk and wool yarns, it would be impossible to dye jute yarns successfully but for the regularity in composition of the fibre. The alternative view that it is made up of cellulose *mixed* with so-called encrusting matters is inconsistent with the foregoing chemical investigations; and a microscopic examination of the fibre mounted, after chlorination, in a solution of sodium sulphite, will satisfy every observer of the uniform distribution of the "potential tannin" throughout the fibre substance, which could scarcely obtain if it were present as an encrusting substance.

To sum up and give definiteness to the view which we have thus developed as more consistent with facts, as well as with the deductions of biologists, we propose to give the name of *Bastose* to this transition modification of cellulose, at the same time observing that as there are many celluloses, so there would be necessarily corresponding forms of *bastose*. This nomenclature may be extended to the aromatic derivatives, to which we propose to give the generic term *Bastin*. Both of these terms may be made specific by means of prefixes derived from the name of the plant from which the fibres are obtained: thus, *e.g.*, we should use the names *Linobastose*, *Corchorobastose*, &c., &c.

It may be urged that we have as yet given no direct proof of the possible conversion of carbohydrates into aromatic bodies. There is, however, no lack of evidence on this point. Hoppe-Seyler (*Berl. Ber.*, 4, 15) for instance, found that by heating starch to high temperatures in presence of water, catechol was formed. The nitrocelluloses have been so often observed to degrade spontaneously into bodies of the pectic class, that Abel says on this point: "These substances have been so frequently obtained that they must be regarded as general products of the gradual decomposition of guncotton;" and meta-pectic acid, the last member of the series, has recently been shown to be resolved by fusion with potassium hydrate (Rochleder, *Zeitschr. f. Chem.* [2], 4, 381) into formic and protocatechuic acids.

* The technological bearings of these researches will be found treated by Dr. O. Witt and C. F. Cross in papers recently communicated to the *Soc. Ind. Mulhouse*.

This fact of the passage of cellulose into pectin,* we may also observe, is in harmony with the interpretation which we have given of Sachsse's equation for the chemical changes involved in lignification. There are also several observations of the direct transformation of cellulose into pectic bodies in nature which have been made by Frémy (*Compt. rend.*, 48, 203), and Vogt (*Sitz. ber. Kais. Acad.*, 48, 689). But perhaps the most conclusive proof of this transformation of carbohydrates into aromatic derivatives, is that which we recently communicated to the British Association (*Chem. Section Reports*, 1881). We found that by the action of concentrated sulphuric acid at 70°, cellulose (dextrin) was converted into a black substance containing 64.4 per cent. C and 4.4 per cent. H.† By the action of chlorate of potash and hydrochloric acid it was converted into the derivative $C_{21}H_{16}Cl_4O_{10}$,‡ exactly resembling in properties as well as in composition the chlorobastin previously described. The formation of the original black substance was attended by that of acetic and carbonic acids, and furfural. This transformation would appear to be closely similar to the resolution of the soluble modification of bastose on distillation with dilute acid, and completes therefore the chemical proof of the possible occurrence of such a resolution of cellulose during and by reason of the life of the plant, as would lead to the formation of astringent substances together with certain more highly oxidised bodies (probably aldehydes, pectic bodies, &c.).

As we indicated, these observations throw light on the formation and composition of coal and other so-called carbonaceous products. Berthelot (*Ann. Chim. Phys.* [5], 17, 139), in discussing the proximate composition of a charcoal formed from cellulose, which he found to contain 20 per cent. of oxygen, uses the following language: "J'ai déjà insisté sur l'existence de ces composés humiques et charbonneux formés par la voie des condensations successives et dont les divers carbones représentent la limite extrême." In corroboration of this view we have obtained from wood-charcoal§ by heating it with nitric acid in a sealed tube, a nitro-compound exactly resembling that obtained from esparto, and from coal (Wigan cannel) a chlorinated derivative containing 26.3 per cent. Cl, and in every respect similar to the compound previously described.

Berthelot has formulated (*Ann. Chim. Phys.* [4], 9 and 19) the laws under which these so-called "carbons" of pyrogenic origin may

* Reichardt maintains (*Arch. Pharm.* [3], 10, 116) the close connection of the pectous substances with the carbohydrates.

† This black substance dries up to a hard compact mass with a shining fracture, and almost indistinguishable from coal.

‡ This body gives a large yield of chloropicrin (10 per cent.) when distilled with nitric acid.

§ This observation was made by Hatchett (*Phil. Trans.*, 1805, 211, 285).

be supposed to be formed, but has not extended his theories to the consideration of the chemistry of coal. Into this subject we do not consider it at present expedient to enter at any length, but would remark that it is at least probable that coals constitute the limiting terms of the series (comp. Balzer, *Vierteljahreschrift Zürich. Naturf. Ges.*, 17, 1, 1872) of successive transformations of cellulose, developed according to the laws which Mills (*Watts' Dict.*, III Supp., p. 593; *Phil. Mag.*, June, 1877) has formulated as those of "Cumulative Resolution."

Reverting to what we term the bastose series of the jute fibre, it is important to consider the evidence as to its being simple or complex. In our original paper we gave several analyses of the chlorobastin, all of which proved singularly constant, although the several preparations were obtained from different specimens of jute, and in one case the fibre had been profoundly modified (structurally) by long boiling with dilute sulphuric acid. Moreover, the remarkable purity of the colour reaction of this derivative, and its invariable characteristics, point to the uniformity in composition of this extreme product of the resolution of the fibre. On the other hand, the isolated cellulose will appear from what follows to be a mixture. In the first place it is different in aggregate composition from the more ordinary forms, (linen, cotton, &c.). The following are the percentages of carbon and hydrogen, determined by combination of different specimens.

- (α .) Specimens obtained as a yield of 80 per cent. of the fibre (chlorine method).
- (β .) Specimens obtained as a yield of 70 per cent. of the fibre (bromine method).
- (γ .) Specimens obtained from fibre previously disintegrated by boiling with HCl, and subsequent treatment by chlorine method.
- (δ .) Specimens obtained from Swedish filter-paper.

	(α)		(β)	(γ)	Calc. $3C_6H_{10}O_5, H_2O$.		(δ)
C	42.7	43.2	43.5	43.0	42.8		44.0
H	6.2	6.2	6.0	5.9	6.3		5.8

An examination of jute cellulose by means of the Schweizer-Pelonze reagent, showed that it differed from ordinary cellulose in another important particular, viz., in being only imperfectly precipitated by mineral acids from its solution in this reagent, whereas linen cellulose was found by Schlossberger (*Lieb. Ann.*, 7, 21), and by Boussingault (*Ann. Chim. Phys.* [4], 13, 231) to be completely precipitated. Three specimens of jute cellulose were dissolved and precipitated, the percentages recovered being 81.7, 89.0, and 89.2 respectively.* The

* On boiling the solution there occurs a still further transformation into the

precipitated cellulose gave on oxidation with alkaline permanganate a large yield of oxalic acid; and the body remaining in solution was isolated and found to be a carbohydrate closely resembling dextrin.

In our original paper we give the results of experiments, showing that jute cellulose, unlike ordinary cellulose, was in part readily transformed into soluble bodies by the action of bromine-water in the cold; and by dilute mineral acids at 60°. On the other hand we showed that if in our chlorination method of estimating cellulose, the action of the gas was followed by treatment with dilute sulphuric acid, before boiling off in alkali, the yield was uniformly increased 3—5 per cent. Subsequent experiments have fully confirmed this: we find moreover that the yield can be still further augmented by allowing the chlorination to proceed at as low a temperature as possible, *e.g.*, by placing the fibre in contact with powdered ice. By the method thus modified we have succeeded in isolating the following percentages of cellulose* :—

80.9	80.6	79.9	82.0	81.3	84.5
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By otherwise varying the process, different percentages can be isolated, which exhibit corresponding variations. From these observations we infer that the isolated cellulose is a mixture of two or more forms, which differ either in aggregation, degree of hydration, or even more fundamentally, and are either wholly or partially products of resolution of the parent substances, *i.e.*, the bastose constituents of the normal fibre.

Frémy (*Compt. rend.*, 48, 862) has endeavoured to establish definite distinctions between certain of the more commonly occurring celluloses. Sachsse (*Farbstoffe*, 150) however points out that any classification of celluloses, based, as Frémy has based his, into "fibrose," "vasculose," &c.,† upon the behaviour of the substances towards acids and alkalis, is rendered nugatory by the mere consideration of the necessary variations, in constitution and composition of these substances, with the age of the tissue which they go to build up. While agreeing with Sachsse in rejecting Frémy's classification, we do not feel ourselves in a position to speak definitely as to the lines

soluble form; thus in one case after 10 minutes' boiling 71.9 per cent., and after 1 hour only 47.1 per cent. was recovered by precipitation.

* The variations exhibited by these numbers are in harmony with our general view of the constitution of the fibre. To increase the yield of cellulose above 75 per cent., the necessary modification of the process must have reference to those constituents, which easily tend to degrade into soluble products, and are therefore far more sensitive to the unavoidable slight variations in the application of the reagents.

† This classification has also reference to the various points or localities of origin of the cellulose within the plant, and is supported by the *à priori* ground for the existence of differentiated celluloses. The differentiations, however, cannot be regarded as affording a basis for chemical classification.

upon which a classification of these bodies should be based ; but it is our intention to apply the results of our researches without delay, to the investigation of this important problem.

Miscellaneous.

Under this head we must include an account of certain observations which, while they bear upon the main points at issue, have only a subordinate place in their logical treatment.

(a.) *Glycolignose and Glycodrupose* (Erdmann, *Lieb. Ann.*, 138, 1 ; and V Suppl., 223).—In our first paper we drew attention in passing to these substances, as calculated to throw light upon our investigations. On examining the stony concretions of pears, we found that they could be resolved in precisely the same way as bastose, into cellulose on the one hand, and an aromatic chlorinated derivative on the other, giving the characteristic colour-reaction with sodium sulphite. We may remark that the experiment of chlorinating a thin section of the fresh fruit, and then plunging it into a solution of this salt, forms a very brilliant demonstration of its structure ; the stony concretions becoming deep purple in colour, while the astringent matters, which towards the peel have a radiating and concentric arrangement, become variously coloured from purple to orange-red ; these colours are beautifully contrasted with the pure white of the cellular substance of the flesh. On further treating a section, thus acted upon, with a dilute solution of ferric chloride, the reds give place to dark olive-greens, the arrangement of which constitutes another beautiful colour effect. On comparing this iron reaction with that afforded by the fresh fruit, a considerable development of tannins will be recognised. The formula given by Erdmann for glycodrupose, $C_{24}H_{36}O_{18}$ (C 49·6 per cent. and H 6·2 per cent.) involves a slightly higher percentage of carbon than is present in normal jute : the drupose ($C_{18}H_{28}O_{12}$) into which, together with glucose, this complex substance is resolved, has a composition similar to that of bastin ($C_{18}H_{24}O_9$).

There can be no doubt therefore that Erdmann's interpretations of his results need correcting by considerations drawn from our researches. The reaction of drupose with dilute nitric acid, whereby it was resolved into cellulose and certain soluble substances (not further examined), is a further proof of its close similarity to bastose, and that the hypothetical equation by which Erdmann represents this proximate resolution, viz. :—



does not adequately represent the chemistry of the change.

(b.) *Origin of Tannins*.—There can be little doubt that Baeyer's

interesting researches (*Berl. Ber.* [5], 25, 280, 1094) on the reactions of the phenols with the aldehydes, constitute an important advance towards the discovery of the immediate origin of the aromatic constituents of plants, more especially of the astringents and colouring matters. The researches in question led Baeyer to conclude that all aldehydes unite with all phenols to form bodies belonging to the group of phenol colouring matters. The observations which have the most direct bearing upon our subject are: (1) that by the action of furfural upon resorcinol in presence of hydrochloric acid, he obtained a substance dissolving in water to a green solution resembling in its optical properties that of chlorophyll; and (2) that formaldehyde and pyrogallol react to form an amorphous compound closely resembling tannin, which in presence of excess of the aldehyde yielded a fugitive bright-red colouring matter.

Our researches have clearly shown that the resolution of plant-substances is generally attended by the liberation of aldehydes, and there have been numerous observations of the presence of phenols in living plants (Gorup-Besanez, *Berl. Ber.*, 4, 15; *N. Repert f. Pharm.*, 23, 180; Kraus, *ibid.*, 22, 273, &c.). In absence of further observations, however, we withhold discussion of this interesting question, contenting ourselves with indicating this as a direction which our future researches must take.

(c.) *Reactions of the Jute Substance under High Pressure*.—(1.) Heated with water for 12 hours at 110° C.; 2.64 grams fibre. Only slightly attacked. Weight of fibre after washing and drying, 2.411; loss 11 per cent.

(2.) Heated with water 10 hours at 120–130°; 4.43 grams fibre. As before, only slightly attacked. Heating continued for another 10 hours. The fibre was thoroughly disintegrated, dark-brown in colour. Solution acid, smelling strongly of burnt sugar.* Weight of modified fibre 3.212 grams, loss 27.5 per cent.

(3.) Heated with water 9 hours at 140°; 4.52 grams raw fibre. Completely disintegrated. Weight of modified fibre 3.498; loss = 22.6 per cent. After chlorination, &c., it yielded 2.691 = 59.5 per cent. cellulose, or calculated on the modified fibre = 76.8 per cent. The modified fibre gave the following percentages on combustion: C = 48.3, H = 5.16†.

(4.) Heated with water and barium carbonate for 9 hours at 135°; 4.457 grams raw fibre. Colour changed to dark-brown, fibre not disintegrated. Some quantity of barium in solution. Yield of modified fibre 3.565 grams = 80 per cent. Cellulose 2.837 = 63.5, or calculated on modified fibre, 79.3 per cent.

* Compare *Report on Rhea Fibre*, Dr. Forbes Watson.

† Compare action of dilute acids, p. 100.

(5.) Heated with 1 per cent. NaOH solution for 10 hours at 120—130°; 4.43 grams raw fibre. Fibre yellowish-brown, but not disintegrated. Yield of modified fibre $3.77 = 85.1$ per cent. Cellulose $3.044 = 68.7$, or calculated on modified fibre, 80.7 per cent.

(6.) Heated with dilute hydrochloric acid (5 per cent.) for 10 hours at 120—130°. The jute was converted into a brownish-black powder, which on chlorination yielded the orange-coloured derivative, giving the characteristic reaction with sodium sulphite; but on boiling with alkali it was completely dissolved, showing that no cellulose survived this treatment. The solution contained only traces of aromatic bodies.

(7.) Heated with dilute sulphuric acid (7 per cent.) 12 hours at 110°. 2.659 gram raw fibre. Entirely disintegrated. Yield of modified fibre $1.857 = 69.8$. Cellulose $1.232 = 46.3$ per cent., or, calculated on modified fibre = 80.7 per cent.

(8.) Heated with solution of acid sodium sulphite (2.6 per cent. SO_2) for 10 hours at 115°. 4.482 grams raw fibre. Perfectly bleached, and somewhat disintegrated. Yield of modified fibre 89 per cent. Cellulose 2.93 grams = 65.4, or, calculated on modified fibre, 73.5 per cent.

(9.) Heated with neutral sodium sulphite (5 per cent.) for 10 hours at 120—130°. 4.444 grams raw fibre. No pressure on opening; solution faintly alkaline; fibre disintegrated. Perfectly bleached; became rose-coloured on exposure to air. Yield of modified fibre 3.609 grams = 81.2 per cent. Cellulose 3.050 grams = 68.7 per cent., or, calculated on modified fibre, 84.6 per cent.

It is not necessary specially to discuss the above results, as without raising any new point, they are in full accord with what has gone before.

(d.) *Reduction of Indigo by Jute.*—It is an interesting observation, as showing the presence in the jute fibre, or perhaps rather the ready development from the parent substance, of strongly deoxidising agents, that powdered indigo-blue is converted into the soluble hydrogenised compound by suspension in a solution of potassium hydrate in contact with raw jute. Pectic acid has previously been observed to exert the same action, and has been successfully employed in the dyeing of wool (Leuchs, *Polytech. Notizblatt*, 1865, 277; *Crookes's Dyeing and Calico Printing*, p. 481). The reduction of indigo by means of bran and lime, which is the principle of the ordinary "vat" used in wool-dyeing, is probably best explained by the presence in the former of the furfural-yielding constituent, especially as the temperature at which the vat is maintained (50° C.) and its general conditions point to this rather than to any fermentation action as the efficient cause of the reduction.

(e) *Reaction of Linseed Oil with Sulphuric Acid.*—When linseed oil is mixed with oil of vitriol, a violent reaction ensues, resulting in

the formation of a viscous black substance, from which water dissolves the substance known as *Hatchett's artificial tannin* (*Watts' Dict.*, 3, 703; *Phil. Trans.*, 1806, 109—146). We found, on examining this black substance, that it was converted by the action of potassium chlorate and hydrochloric acid into a golden-yellow chlorinated derivative, melting below 100°. This body resembles the chlorobastin in properties and reactions, and affords a verification of the close chemical connection which biologists have assumed to exist between the physiologically equivalent carbohydrate and fats.

(f.) *Additional Observations on the Chlorobastins.*—On carefully heating the crude product from esparto, a small sublimate of golden-yellow plates was obtained, which gave a dark purple-blue coloration (compare Wichelhaus, *Berl. Ber.*, 14, 952) with dimethylaniline; this reaction is known to be characteristic of the chloroquinones, and gives support to our view of the probable constitution of the chlorobastins.

We have made observations on the absorption spectrum of the coloured solution obtained by treating the freshly prepared chlorobastin with sodium sulphite, but were unable to distinguish any characteristic feature.

It may be further observed that bastose, treated with chromic acid solution, gives with sodium sulphite a colour reaction similar to that of the chlorobastin.

Chlorobastin when strongly heated evolves a "permanently" gaseous chlorine-compound, which was found to burn with a green flame. This body is still under investigation.

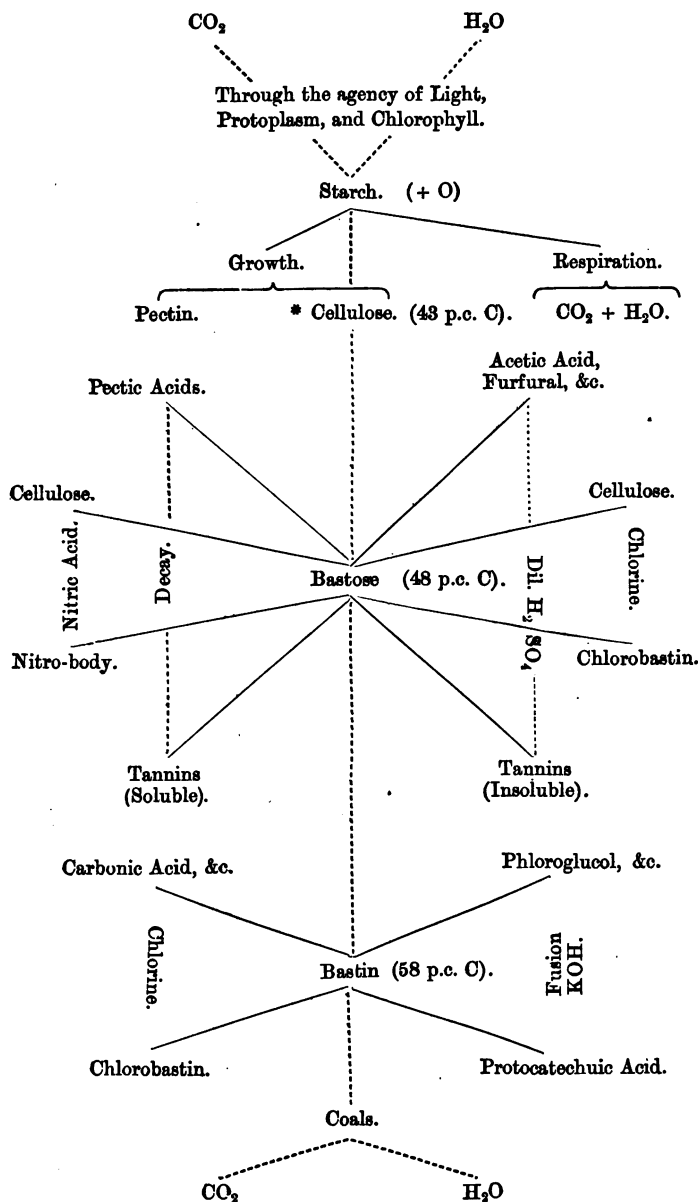
Conclusion.

We have attempted to give, in the accompanying sketch, a diagrammatic survey of the main results of our researches. It is of course very imperfect, but the main feature of the passage of cellulose into aromatic bodies allied to the tannins, for the actual occurrence of which in the life of the plant we have adduced so much evidence, is clearly represented.

The imperfections are due to the dynamic condition of the transformation considered in relation to the statical observations by which alone it can be investigated, and to the insufficient nature of these.

That these, moreover, are statistical rather than molecular, needs no further explanation or justification. Neither need we allude specially to the fact that nitrogen plays no essential part in this chapter of plant chemistry, *i.e.*, so far as our observations are concerned.

Our researches are a further contribution, however meagre, to the ideal arrangement of the carbon-compounds, *viz.*, according to their synthesis and transformations in that most marvellous laboratory, the living plant.



* Isolated jute cellulose contains 43 p.c. C and 6 p.c. H, and is represented by the formula $n(3C_6H_{10}O_5H_2O)$.

XVII.—*A New Apparatus for the Determination of Melting Points.*

By C. F. CROSS and E. J. BEVAN.

As it is well known that the behaviour of liquids in capillary tubes is controlled by laws different from those which regulate them under ordinary conditions, it is obvious that the usual method of determining melting points is consequently open to at least one serious objection; and as the ascertaining of the exact melting point of a substance thereby is a matter of some little difficulty and trouble, a method which is not open to such objections must be regarded as a desideratum. We believe that the following method will recommend itself on this account.

The essential parts of the apparatus consist of a small platform, Fig. I (actual size), made of very thin sheet-iron (the thin sheets used for ferrotypes are suitable) or silver (platinised), having an opening A, cut for the purpose of receiving the bulb of a thermometer, and a small indentation B, about 1.5 mm. deep and 2 mm. in diameter, and a glass float (Fig. II) having a thin piece of platinum wire sealed into one end, flattened, and bent in the shape of the letter L, as shown.

To make an observation, a very small quantity of the substance is melted in the indentation (B, Fig. I) of the platform, and while it is still liquid, the platinum wire of the float is placed in it, and allowed to become fixed by the solidification of the substance. Thus arranged, a thermometer is placed in the opening A, and the whole disposed as in Fig. III in a small beaker containing mercury (or other liquid). The mercury is now gently heated, the thermometer being carefully



FIG. I.



FIG. II.

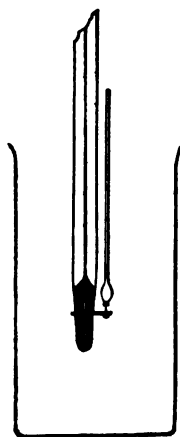


FIG. III.

watched. As soon as the melting point is reached, the float, being liberated, rises instantly to the top of the mercury.

The special advantages of this method, in addition to those already alluded to, are these:—(I) The substance being entirely surrounded by the mercury and the metallic platform is certain to be of exactly the same temperature as the thermometer; (II) on account of the perfect conductivity of the mercury no stirring is necessary; and (III) as the sudden rise of the float at the melting point forces itself upon the attention of the operator, his observations can be entirely confined to the thermometer.

The following determinations may be cited as showing the correctness of the method and its applicability to a very wide range of temperature. The numbers have a purely relative value, as the thermometer was not corrected in any way, nor were the substances specially purified:—

Purified paraffin.	Resorcinol.	Mercuric chloride.	Sodium nitrate.
52.7°	105.0°	257.0°	286.0°
52.4	105.1	259.0	287.0
52.4	105.0	259.0	287.0
52.6	105.5	—	288.0
52.7	104.5	Mean 258.3	286.0
52.3	105.0		—
Mean 52.5	105.0		Mean 286.8

In order to prove the correctness of the method, the melting point of the paraffin used in the above determinations was observed by the inverse method of immersion of the thermometer in a half melted mass, as in the determination of the melting point of ice. In three experiments the values 52.5, 52.4, and 52.5 were obtained.

Notes.

(a.) In order to prove that no stirring was necessary, the following experiment was made:—A test-tube, 3 ins. in diameter and 8 ins. long, was filled with mercury and fitted with two thermometers, the bulb of one being at the top and that of the other at the bottom of the mercury. On gently heating it was found that both thermometers indicated exactly the same temperature. This being so, if very accurate results were required, the thermometer could be immersed in the mercury to any extent, and thus the error due to the exposure of the stem could be eliminated.

(b.) Since writing the above, we have seen a notice of a melting point apparatus described by C. H. Wolff (*Arch. Pharm.* [3], 6, 534). His arrangement, which is a modification of one proposed by G. Löwe, consists in coating a thin platinum wire with the substance whose melting point is to be observed, and making it part of an

electrical circuit in which a bell is placed. The connection between the two is made by a mercury-bath containing a thermometer. If now the bath be heated the substance melts, and the platinum wire becomes electrically connected with the bell, and thus the melting point is announced.

XVIII.—On the Reaction of Chromic Anhydride with Sulphuric Acid.*

By C. F. CROSS and A. HIGGIN.

It is well known that on heating chromic anhydride with concentrated sulphuric acid, oxygen is evolved, and the chromium, passing into a lower state of oxidation, unites with the acid to form insoluble compounds. We have searched chemical literature for an account of these bodies, and finding none, we undertook their investigation.

To prepare these bodies for analysis, it is simply necessary to digest the chromic anhydride with excess of sulphuric acid at a temperature somewhat below the boiling point of the latter. When the evolution of gas has ceased, the chromium will be found to be almost entirely converted into the insoluble sulphate, which is deposited in the form of a fine mud of a lavender-grey colour; this is well washed and dried at 110°.

The analysis of the sulphate by the ordinary method of fusion with alkaline salts, and subsequent estimation of the constituents, led to such extremely variable results, that it had to be abandoned in favour of the following more simple and direct process. We found that by ignition with boric anhydride, the sulphuric acid, ($\text{SO}_3 + \text{H}_2\text{O}$), could be accurately estimated by the loss of weight, and on treating the residue with an alkali the chromium was isolated as the pure sesquioxide. The following were the results of an analysis by this method:—

(1.) 1.1470 gram lost 0.7500 on ignition and yielded 0.3977 Cr_2O_3 .

(2.) 0.5210 „ yielded 0.1818 „

Cr_2O_3	34.67	34.9
$\text{SO}_3 + \text{H}_2\text{O}$	—	65.3

100.2

From the conditions of its formation it was evident that the chromium in the original sulphate is in the lower state of oxidation; by this analysis, therefore, all its constituents were accounted for.

The separation and estimation of the water was accomplished by

* Our attention was directed to this reaction by Dr. Otto Witt, who obtained the insoluble sulphates described by us, in the process of oxidising the carbonaceous matters in a diatomaceous mud, by means of $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 .

igniting the substance mixed with lead oxide in a combustion-tube, connected with a chloride of calcium absorption-tube, with observance of the usual precautions.

The following numbers were obtained:—

0.6945 gram gave 0.0500 H_2O = 7.2 p. c. }
 0.1780 " 0.0130 " = 7.8 " } Mean = 7.25 p. c.

The composition of this body is therefore represented by the following numbers:—

	Per cent.	Calc. $4\text{Cr}_2\text{O}_3 \cdot 7\text{H}_2\text{O} \cdot 13\text{SO}_3$ or $2(2\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3) \cdot 7\text{H}_2\text{SO}_4$
Cr_2O_3	34.78	34.40
SO_3	58.17	58.50
H_2O	7.25	7.09
	<hr/> 100.20	<hr/> 99.99

A second preparation gave on analysis the following results:—

0.2936 gram lost 0.1982 (B_2O_3 method).
 0.2100 " 0.1424 (" " ").
 *0.3490 gram yielded 0.1176 Cr_2O_3 } by fusion with Na_2CO_3 .
 0.4090 " 0.1376 " }
 0.5470 " 0.0370 " by ignition with PbO .

Cr_2O_3	33.7	33.64
SO_3	60.7	60.90
H_2O	6.8	6.80
	<hr/> 101.2	<hr/> 101.34

These and other determinations showed that the substances in question are only approximately constant in composition. The formula given above may be taken as representing the average relation of the constituents.

Respecting the properties of these interesting bodies, it only remains to add that they are entirely insoluble in water, and are attacked with difficulty by the alkaline hydrates (solutions). They cannot be made the basis of a quantitative method of estimating CrO_3 , since they are somewhat variable in composition, and their formation is always attended with the conversion of a small portion of the chromium into the ordinary soluble sulphate.

Potassium dichromate reacts similarly with sulphuric acid, but in this case the precipitates are coarsely granular, of a grass-green colour, and contain potassium.

* Although twice precipitated, the Cr_2O_3 was still impure, the numbers being about 1 per cent. too high, and it was these results which led to the substitution of the method of isolation after fusion with B_2O_3 .

The following analyses may be cited in illustration of their composition:—

Ignition with B_2O_3 —

0.2473 gram lost 0.1633 = 66.03 per cent.	} Mean 66.
0.2300 " 0.1520 = 66.08 "	
0.1598 " 0.1054 = 65.90 "	
0.4200 " 0.2790 and yielded 0.112 Cr_2O_3 .	
0.5340 gram yielded..... 0.141 "	

Ignition with PbO —

	1.0657 gram lost 0.0756	
	1.0853 " 0.0759	
Cr_2O_3	26.66	26.40
H_2O	7.09	6.99
SO_3	59.31	59.01
K_2O (by difference)	6.94	7.60
	<hr/> 100.00	<hr/> 100.00

A second preparation gave the following results:—

Ignited with B_2O_3 —

0.5190 gram lost 0.3510 and yielded 0.1440 Cr_2O_3 .

Ignited with PbO —

1.1230 gram lost 0.0828.

Cr_2O_3	27.74
H_2O	7.37
SO_3	60.33
K_2O	4.56
	<hr/> 100.00

These sulphates are characterised therefore by variability in composition. They lose on ignition over the blowpipe about 50 per cent. of their weight; whereas the sulphates prepared from the pure anhydride lose 63—64 per cent., i.e., their water, and nearly the whole of the sulphuric anhydride.

XIX.—On Some Decompositions Produced by the Action of Chloride of Aluminium.

By C. FRIEDEL and J. M. CRAFTS.

THE last number of the Journal contains an account of the action of chloride of aluminium on chlorocarbonate of ethyl dissolved in benzene. Mr. Rennie appears to have overlooked a notice on this subject in the *Compt. rend.* of the 18th June, 1877, in which we described

exactly the same results that he has subsequently obtained, viz., the transformation of chlorocarbonic ether into CO_2 and $\text{C}_2\text{H}_5\text{Cl}$, and the formation of ethyl- and diethyl-benzene, by the action of this latter body upon benzene in presence of chloride of aluminium.

We found in general that compounds containing the group OH or OR, i.e., alcohols, phenols, acids, and their ethers undergo decomposition with chloride of aluminium, and the reactions which we have described are usually impossible in the presence of such bodies.

We are engaged at present in the study of the destructive action of chloride of aluminium upon hydrocarbons, and find that, under many circumstances, this curious reaction fixes a limit to synthetic operations. Thus higher homologues of benzene lose their side groups and tend to be resolved to C_6H_6 when heated with chloride of aluminium. Hex-methylbenzene, for example, can easily be reduced to durene and simpler hydrocarbons.

We have already published some results obtained with petroleum and with naphthalene, and are pursuing the study of a series of compounds rich in hydrogen, which can be easily obtained by heating chloride of aluminium with naphthalene; it is to be hoped that some of them may throw additional light on the structure of naphthalene.

As an example of the manner in which the destructive action of chloride of aluminium sets a limit to synthesis, may be mentioned the case of triphenylmethane, which, even in solution in benzene, is easily reduced in considerable part to diphenylmethane by heating to 75° with an equal weight of chloride of aluminium: consequently the conditions recommended by Messrs. Fischer (*Annalen der Chemie*, 194, 242) for the preparation of triphenylmethane are not the most favourable; not only can the proportion of diphenylmethane upon which these authors insist be greatly reduced, but also the quantity of triphenylmethane augmented in a well-conducted operation.

It is to be noted that the chloride of aluminium should be quite anhydrous, or at least it should not leave more than 5 per cent. of residue on volatilisation. The presence of hydrated products arising from the action of moisture on chloride of aluminium not only enfeebls its activity in a remarkable degree, but also frequently gives rise to complicated processes in which the oxygen seems to favour the formation of condensed products by a partial combustion. This action does not appear improbable if the theory proposed by us of the formation of a compound of chloride of aluminium with hydrocarbons similar to $\text{ZnC}_2\text{H}_5\text{I}$ is accepted.

It may be added that commercial chloride of aluminium always contains perceptible quantities of oxychloride of carbon, and frequently small quantities of sulphuretted compounds.

XX.—*Chemical Examination of the Buxton Thermal Water.*

By J. C. THRESH, B.Sc.

THE results of the analyses of the sinter deposited by the above water, and of the gases held in solution and evolved at the spring having already been communicated, the present paper treating of the saline constituents completes my examination of this mineral spring.

During the present autumn advantage was taken of an opportunity for determining the flow of water, the reservoirs having been emptied to allow of the baths, &c., being cleaned. By careful measurement the total capacity of the three reservoirs and bath was found to be 2838 cubic feet. From the time when the outlet leading to the drains was closed to the time when the water reached the overflow level was 2 hrs. 55 min. Hence the flow per minute is 16.1 cubic feet, or 101 gallons. This, however, does not represent the whole of the flow from the thermal springs, as the water from all the springs does not flow into these tanks, the water supplying the pump-room being derived from a spring flowing into a distinct reservoir. Some, also, appears to run to waste, but there is little doubt that the total outflow does not greatly exceed the amount stated.

Density of the Water.—On account of the small amount of saline matter present in this mineral water, it was necessary to collect and evaporate large quantities of it. The water was collected in stoppered winchesters, and as it was found impossible to fill these at the mouth of the springs when the tanks were emptied, they were filled in the large bath immediately over the spring yielding the largest proportion of gas. At the time of filling, the water had been flowing through the bath fully twelve hours, without being disturbed by bathers. The capacity of the bottles at a known temperature having been ascertained, it was only requisite to determine the density of the water to find the weight of water employed.

A 50 c.c. specific gravity flask filled with well-boiled distilled water, held at 15° C., 49.9870 grams, and at 14° C., 49.9954 grams.

From equation—

$$C = \frac{w}{d} (1 - ta).$$

we have in both cases $C = 50.029$ c.c. at 0° C.

The flask filled with spring water, at 25.8° C., held in one experiment—

(1)	49.8890 grams, in another	(2)	49.8874 grams.
	Density at 25.8° C.	(1)	0.99688 "
	"	(2)	0.99684 "
	Mean		0.99686 "

The density of pure water at this temperature being 0.99695 (Rossetti), we have 0.99992 as the density of the thermal water, compared with that of pure water at the same temperature. As both the carbon dioxide and saline constituents tend to increase the density of a water, the presence of nitrogen in solution would appear to have a directly opposite effect.

The mode of procedure adopted in this investigation is that recommended by Bunsen in his "Instruction für die Ausführung der vom Grossherzogl. Bad. Ministerium des Innern angeordneten chemischen Untersuchung der Badischen Mineralwässer," the process in nearly all cases being those recommended therein.

21480.4 grams of the water were evaporated in a platinum dish on the water-bath to dryness, care being taken to avoid loss by spitting, access of dust, &c. The residue was kept for several hours on the water-bath, and then treated with successive small quantities of cold water. The aqueous solution was passed through a filter, into a stoppered Schuster's burette, avoiding splashing, and the insoluble portion finally transferred to the filter, washed to 1/10000, and dried at 100° C.

Analysis of the Soluble Portion.—(A.) The fluid in the burette was divided into 5 accurately weighed portions.

- (1.) The sulphuric acid was estimated by precipitation with barium chloride, &c., the resulting barium sulphate being digested repeatedly with water acidulated with hydrochloric acid, until a constant weight was attained.
- (2.) In another portion the calcium and magnesium were determined—the magnesium in the ammonium oxalate precipitate, and the calcium in the precipitate produced by ammonium phosphate being ascertained.
- (3.) In estimating the chlorine, the silver chloride was collected in a porcelain crucible, the filter-paper through which the wash water was passed being burnt in a tared coil of platinum wire.
- (4.) In the fourth portion the sodium and potassium were determined. The boiling solution was precipitated with baryta-water, evaporated to dryness in a platinum dish on the water-bath, the residue exhausted with a small quantity of water and filtered. The excess of baryta was removed by repeated treatment with ammonia and ammonia carbonate, evaporation

and ignition. The solution freed from ammonia was next concentrated and digested for two hours on the water-bath, with a little freshly precipitated mercuric oxide, evaporated to dryness, gently ignited, the residue exhausted with water, the solution evaporated to dryness in a small platinum crucible, and the residue gently ignited and weighed.

The fused mass was next moistened with hydrochloric acid, dried and weighed. The weight was unaffected by this treatment.

The residue was dissolved in water, and the solution divided into three accurately weighed portions. In one the chlorine was estimated, in another the potassium and magnesium (after removal of the excess of platinum by hydrogen), the third being kept as a reserve.

(5.) The fifth portion was reserved.

Analysis of the Insoluble Portion.—(B.) In this portion the carbon dioxide, silica, sulphuric acid, barium sulphate, calcium, magnesium, iron and manganese, were estimated.

The winchesters in which the water had been collected were rinsed with dilute hydrochloric acid, the rinsings transferred to the platinum dish in which the water had been evaporated, and evaporated to perfect dryness. In this residue the trace of silica was estimated, and the acid solution precipitated boiling by sodium carbonate, the precipitate, after washing and drying, being added to the insoluble water residue. In the filtrate, the sulphuric acid and magnesia were determined. The carbon dioxide, equivalent to the sulphuric acid was deducted from the amount of that substance found in (B), whilst the equivalent to the magnesia is added thereto.

Estimation of the Carbon Dioxide.—The dried residue (B) was transferred to a small flask, fitted with bulb acid tube, and a long calcium chloride tube, and the whole weighed. After all the gas had been liberated the acid fluid was raised to the boiling point, then allowed to become perfectly cold, and a very slow current of dry air, free from carbonic acid, aspirated through the apparatus, for about an hour. The heating and aspirating were repeated until a constant weight was attained.

Silicic Acid, Barium Sulphate, and Organic Matter.—The fluid remaining in the flask was evaporated to dryness, treated with acid, passed through a filter, the impure silica exhausted with alcohol and ether, and the organic matter thus removed and estimated. The ignited silica was treated with warm moderately concentrated solution of soda, when a residue consisting of barium sulphate remained, the weight and purity of which were duly ascertained. The filtrate from

the silica was transferred to a weight-burette and divided into three portions.

In (1) the sulphuric acid was determined.

In (2) the iron, manganese, calcium, and magnesium were estimated. After oxidation by boiling with a little bromine-water, the iron (with trace of calcium phosphate, and possibly of alumina) was precipitated by ammonia, redissolved and reprecipitated. The impure Fe_2O_3 thus obtained was dissolved in acid, and upon addition of ammonium molybdate, gave a very slight precipitate, indicating the presence of a trace of phosphate too minute for estimation.

The acidified filtrate, after concentration, was treated with ammonia and ammonium sulphide, and the precipitated manganese determined as Mn_2O_4 .

The filtrate from the manganese precipitate was acidified, concentrated on the water-bath, the sulphur filtered out, and the calcium and magnesium determined as in the soluble portion.

Total Estimation.

10,740.1 grams of water were evaporated to dryness, and the residue treated at once with hydrochloric acid to separate *silica* and *barium sulphate*. The acid filtrate was divided into three portions, *a*, *b*, and *c* :—

(a.) In this portion the *sulphuric acid* was determined.

(b.) Used for estimating the *iron, manganese, calcium, and magnesium*. The impure ferric oxide here obtained was dissolved in acid, the iron reduced to the ferrous state, and determined volumetrically by aid of a very dilute solution of permanganate of potassium.

In the ammonium oxalate precipitate traces of barium and strontium were found. The ignited oxide was treated with nitric acid, the dry nitrate digested with absolute alcohol, the solution filtered off, the minute residue washed with water, and the fluid evaporated to dryness. The barely perceptible residue was taken up on a strip of moist filter-paper, and after burning the paper, the ash was examined for barium and strontium by the spectroscope. Momentary indications were obtained of strontium, but the spectrum of barium was very distinct.

(c.) Reserve.

For the estimation of the total *chlorine*, 3169.7 grams were evaporated to dryness, and the solution obtained by exhausting the residue with water, was precipitated with silver nitrate.

The total *alkalis* were determined in the residue resulting from

evaporating 8013.9 grams of the water, the results being checked as in the former case by the estimation of the chlorine in an aliquot part of the mixed chlorides.

Total Carbon Dioxide.—The water used for this determination was collected in two flasks, each containing 50 c.c. of a solution of 1 part of crystallised chloride of calcium in 5 parts of distilled water and 10 parts of ammonia solution, sp. gr. 0.96. This mixture had been made over two months, and was carefully filtered immediately before use. The flasks were fitted with doubly perforated stoppers. Through one opening was passed a short piece of glass tube, whilst the other was connected with a long tube, kept closed with the thumb whilst the flasks were being sunk. Upon removing the thumb, the water flowed into the flasks, and when the latter were full up to the bottom of the neck, the thumb was again pressed on the end of the glass tube, and the flask withdrawn. A mark being made on the necks of the flasks at the level of the liquid, the quantity used for the analysis was readily ascertained.

The flasks were kept on the water-bath for several hours, then kept for more than one hour immersed in boiling water, and the clear fluid rapidly filtered off by aid of the filter-pump. As much as possible of the precipitate was transferred to a small flask of about 150 c.c. capacity. The crystalline matter on sides of the flasks was dissolved in dilute hydrochloric acid, reprecipitated boiling with slight excess of sodium carbonate, and the supernatant fluid filtered off. The precipitate was well washed, collected on the filter, and the latter with its contents transferred to the flask containing the remaining portion of the carbonates. The carbon dioxide was then liberated by hydrochloric acid, and after passing over calcium chloride and pumice with sulphate of copper, was absorbed in Geissler's bulbs containing solution of caustic soda, and attached to a soda-lime tube.

In the filtrate from the sodium carbonate precipitate, the sulphuric acid and magnesia were estimated, and the requisite corrections afterwards made.

The total carbon dioxide thus found is in excess of the amount found in any of the determinations made in the spring, so also is the quantity of the combined acid, but the free carbon dioxide comes out approximately the same in both analyses. As will be seen on inspection of the table at the end of this paper, comparing the various analyses of the thermal water, the total carbon dioxide now approaches nearly to the amount found by *Hehner* in 1876, whilst the prior analysis agreed closely with the results of *Playfair* (1852), and of *Muspratt* (1860). The probable cause of this discrepancy and of the variation in the composition of the water, as shown by these analyses, will be again referred to.

To detect, and, if possible, estimate the fluorine, boracic acid, iodine, bromine, lithium, and other rare metals, 42,687 grams of the water were evaporated to dryness, with addition of a little sodium carbonate. The residue was exhausted with hot water, and then with cold dilute hydrochloric acid, there being thus obtained (C) an aqueous solution, (D) an acid solution, and (E) a residue insoluble in dilute hydrochloric acid.

Examination of (C).—This measured 220 c.c., and was divided into three portions of 50, 50, and 120 c.c. respectively.

Bromine and Iodine.—50 c.c. were placed in a small stoppered bottle, and a little chloroform added after acidifying the fluid with hydrochloric acid. Standardised chlorine-water was now dropped in, but not the slightest coloration was perceptible. For still greater certainty the solution was rendered alkaline with sodium carbonate, evaporated to dryness, gently ignited, and the residue dissolved in a small quantity of water, acidified, and filtered into a white dish. The chlorine-water was now dropped into the heated fluid, but no indication of the presence of either iodine or bromine was observable.

Boracic Acid.—To the second 50 c.c. were added magnesium chloride, ammonium chloride, and excess of ammonium carbonate, the mixture being evaporated to dryness, and the residue ignited. This was exhausted with hot water, and the filtrate submitted to a repetition of the above treatment. The two residues thus obtained were examined before the spectroscope for boracic acid, but with negative results.

Cesium, Rubidium, and Thallium.—The filtrates from the residues obtained in searching for boracic acid, and the solution used in the examination for iodine and bromine were evaporated to a small bulk and precipitated with excess of platinic chloride. After 24 hours the clear fluid was poured off, and the residue boiled repeatedly with just sufficient water to cover it, the hot supernatant fluid being each time decanted. The whole of the precipitate ultimately dissolved, but from time to time portions were examined before the spectroscope, but no trace of these metals was found.

Lithium.—The remaining 122 c.c. were treated with excess of baryta-water, then with ammonium carbonate, filtered, evaporated to dryness, and ignited. The residue was moistened with hydrochloric acid, dried, and exhausted with alcohol. The filtrate, upon evaporation, left a residue in which the spectroscope showed a trace of lithium, but evidently the quantity was too small for estimation.

Examination of (D).—This solution, saturated with sulphuretted hydrogen, and kept in the hot water-oven for several weeks, deposited a fawn-coloured precipitate. This, when digested with ammonium sulphide, left a black-brown insoluble sulphide, and yielded a brown solution. This fluid was acidified with hydrochloric acid, and the

precipitate fused with sodium carbonate and potassium nitrate, and examined for molybdenum, but with no decisive result. The insoluble sulphide proved to be lead, and was estimated as sulphate.

The filtrate from the hydric sulphide precipitate contained traces of iron, manganese, and calcium phosphate.

Examination of (E).—This residue was examined for fluorine, by fusion with four times its weight of sodium carbonate, exhausting the melt with water, and freeing the solution from silica by digestion with ammonium carbonate. The filtrate was nearly neutralised with hydrochloric acid, calcium chloride added, and the liquid evaporated to dryness. The residue, after gentle ignition, was washed with water and dilute acetic acid, then dried, ignited, and weighed. After treatment with strong sulphuric acid and ignition, the fluoride of calcium was estimated from the increase in weight. The escaping vapour etched glass.

Estimation of Ammonia and Nitric Acid.—Upon attempting to estimate these substances by Bunsen's method, it was found that they were present in too small proportions for accurate measurement by his process. Half a litre of the water therefore was rendered slightly alkaline with sodium carbonate, and the ammonia in the distillate estimated with Nessler's solution in the usual way. After concentrating the water in the retort by evaporation to about 25 c.c., 15 grams of recently ignited pure caustic potash was introduced, together with six zinc-iron spirals. The tubulure of the retort was filled up to the contracted portion in its middle with moistened fragments of glass, and a glass tube, bent at right angles, and closed with a caoutchouc valve dipping into a little water, fitted to the end. After standing 20 hours, the retort was placed on the water-bath for two hours, then 150 c.c. of water were poured into it, and the ammonia was distilled over and estimated.

Nitrous acid had previously been sought for, but not a trace could be detected.

TABLE A.—Total Estimation in Grams.

Quantity of water employed.	Product (with impurities).	Weight of solution.	Portion of solution weighed off.	Precipitate obtained.	Impurities in the precipitate.	Calculated for 10,000 parts of water.	
						Impure products.	Impurities.
SiO ₂ , MgO, CaO, H ₂ SO ₄ .							
10740·1	{ 0·1508 SiO ₂	{ 81·522 {	{ 14·8540 18·3597 {	{ — 0·0760 BaSO ₄ 0·1932 CaO..... 0·2137 Mg ₂ P ₂ O ₇ ..	{ 0·0064 BaSO ₄ — 0·006 Mg ₂ P ₂ O ₇ 0·0009 CaO ..	{ 0·140410 SiO ₂ 0·338360 BaSO ₄ ... 0·798730 CaO..... 0·883497 Mg ₂ P ₂ O ₇	{ 0·00596 BaSO ₄ — 0·02478 Mg ₂ P ₂ O ₇ 0·00372 CaO
KCl and NaCl.							
8013·9	0·4969 KCl + NaCl	{ 17·777 {	{ 6·6318 { 6·5376 {	{ 0·0737 PtCl ₄ 2KCl 0·0012 Mg ₂ P ₂ O ₇ .. 0·4384 AgCl NaCl estimated (by diff.)	{ — — —	{ 0·24718 PtCl ₄ 2KCl — 1·5109 AgCl	{ — 0·00401 Mg ₂ P ₂ O ₇ —
Cl.							
3169·7	—	—	—	0·4789 AgCl	—	1·5109 AgCl	—
CO ₂ .							
1526·0	0·3197 CO ₂	—	—	Filtrate from { Na ₂ CO ₃ ppt. gave {	{ 0·0015 BaSO ₄ 0·0022 Mg ₂ P ₂ O ₇	{ 2·0950 CO ₂	{ 0·0098 BaSO ₄ 0·0144 Mg ₂ P ₂ O ₇
996·9	{ 0·000011 NH ₃ 0·000274 HNO ₃ 0·012100 CaF ₂	{ — — —	{ — — —	{ — — —	{ — — —	{ 0·00011 NH ₃ 0·00275 HNO ₃ 0·00283 CaF ₂	{ — — —
42687·0	{ 0·002700 PbSO ₄	{ —	{ —	{ —	{ —	{ 0·00063 PbSO ₄ ..	{ —

TABLE B.—*Soluble and Insoluble Portions.*

	Portion weighed off.	Product with impurities.	Impurities.	Impure products calculated to 10,000 parts of water.	Impurities calculated to 10,000 parts of water.
A. Portion soluble in Water.					
Weight of solution 109·1364 grams from 21480·4 grams water.	15·1814	0·1078 BaSO ₄	—	0·36078 BaSO ₄	—
	12·8082	0·3772 AgCl	—	1·49629 AgCl	—
	{	0·0045 CaO	—	0·00798 CaO	—
		0·0933 Mg ₃ P ₂ O ₇	0·0018 CaO	0·16400 Mg ₃ P ₂ O ₇ ..	0·003192 CaO
	35·3020	0·4356 KCl + NaCl {	Portion of solution employed = 2769·0 grams water. 0·0682 PtCl ₂ ·2KCl .. 0·0047 Mg ₃ P ₂ O ₇	0·62698 KCl + NaCl —	0·2463 PtCl ₂ ·2KCl 0·01697 Mg ₃ P ₂ O ₇
B. Portion insoluble in Water.					
By action of hydro- chloric acid.	—	0·3103 SiO ₂	—	0·14446 SiO ₂	0·00778 BaSO ₄
	—	1·9460 CO ₂	—	0·90593 CO ₂	—
	{	0·0003 SiO ₂	—	0·00015 SiO ₂	—
		0·0014 BaSO ₄	—	0·00065 BaSO ₄	—
0·0012 Mg ₃ P ₂ O ₇		—	0·00055 Mg ₃ P ₂ O ₇ ..	—	
Filtrate from Na ₂ CO ₃ precipitate	32·9924	0·0113 BaSO ₄	—	0·01629 BaSO ₄	—
	{	0·0016 Fe ₂ O ₃	—	—	—
		0·0013 Mn ₂ O ₄	—	—	—
		0·5796 CaO	0·0386 Mg ₃ P ₂ O ₇	0·79987 CaO	0·05326
Solution in acid, 102·1610	34·4675	0·5048 Mg ₃ P ₂ O ₇	0·0017 CaO	0·69655 Mg ₃ P ₂ O ₇ ..	0·00235

TABLE C.—*Products free from Impurities.*
Calculated as obtained from 10,000 grams of Water.

	A. Soluble portion.	B. Insoluble portion.	A + B. Total.	Total estimation.	Mean.
SiO ₂	—	0·13668	—	0·13445	0·13556
CO ₂	—	0·90593	—	2·08900	—
BaSO ₄	0·36078	0·01694	0·37772	0·38886	0·38804
AgCl	1·49629	—	—	1·51090	1·50360
HNO ₃	—	—	—	0·00275	—
CaF ₂	—	—	—	0·00283	—
CaO.....	0·01117	0·78303	0·79420	0·79352	0·79386
Mg ₂ P ₂ O ₇	0·15811	0·74547	0·90358	0·90142	0·90250
NaCl	0·53708	—	—	0·54092	0·53900
(KCl) ₂ PtCl ₄	0·24630	—	—	0·24718	0·24674
NH ₃	—	—	—	0·00011	—
Fe ₂ O ₃	—	0·00221	—	0·00218	0·00219
Mn ₂ O ₄	—	0·00179	—	0·00198	0·00189
BaSO ₄	—	0·00778	—	0·00596	0·00687
PbSO ₄	—	—	—	0·000633	—
Al ₂ O ₃	—	—	—	0·000683	—
Ca ₃ (PO ₄) ₂	—	—	—	0·00379	—
Organic matter	—	0·00275	—	trace	—
Lithium	—	—	—	—	—
Strontium	—	trace	—	—	—

TABLE D.

I.	II.	III.	IV.	V.	VI.
SOLUBLE PORTION.—1. <i>Estimation of Acids.</i>					
$\frac{1}{2}$ BaSO ₄	0·36586	0·0031367	} 0·0136686 = S	0·003114	} 0·013570
$\frac{1}{2}$ AgCl	1·50360	0·0104883		0·010413	
$\frac{1}{2}$ HNO ₃	0·00275	0·0000436		0·000043	
2. <i>Estimation of Bases.</i>					
NaCl	0·53900	0·0092121	} 0·0134740 = S ₁	0·009278	} 0·013570
$\frac{1}{2}$ PtCl ₄ ·2KCl	0·24674	0·0010111		0·001018	
$\frac{1}{2}$ CaO	0·01115	0·0003986		0·000401	
$\frac{1}{2}$ Mg ₂ P ₂ O ₇	0·15793	0·0028457		0·002867	
$\frac{1}{2}$ NH ₃	0·00011	0·0000065		0·000006	
INSOLUBLE PORTION.—1. <i>Estimation of Acids.</i>					
$\frac{1}{2}$ BaSO ₄	0·01718	0·0001743	} 0·0458878	0·000147	} 0·041469
$\frac{1}{2}$ SiO ₂	0·13556	0·0044887		—	
$\frac{1}{2}$ CO ₂	0·90593	0·0411790		0·041249	
$\frac{1}{2}$ CaF ₂	0·00284	0·0000728		0·000073	
2. <i>Estimation of Bases.</i>					
$\frac{1}{2}$ CaO	0·76271	0·0279437	} 0·0414679	0·027944	} 0·041469
$\frac{1}{2}$ Mg ₂ P ₂ O ₇	0·74457	0·0134158		0·013416	
$\frac{1}{2}$ Fe ₂ O ₃	0·00219	0·0000647		0·000055	
$\frac{1}{2}$ Mn ₂ O ₃	0·00189	0·0000495		0·000050	
$\frac{1}{2}$ PbSO ₄	0·00063	0·0000042		0·000004	

From the mean values obtained as shown in Table C from the results of the "total examination," and of the analyses of the "soluble" and "insoluble" portions are calculated the most probable values of the products obtained in the latter. Let "A" be the weight of any precipitate obtained in the analysis of the portion soluble in water, calculated to parts in 10,000, "B" that of the precipitate from the insoluble portion, and "M" the mean value of A + B obtained as above, the portions "A₁" and "B₁" corresponding to this mean value are readily found from the equations—

$$A_1 = \frac{A}{A + B} M, \quad B_1 = \frac{B}{A + B} M.$$

The values thus found are placed in the second column of Table D.

As a further check, each of these numbers is divided by the *equivalent* weight of the substance as deduced from its chemical formula, and the product placed in column III. In the soluble portion the sum of the numbers so obtained from the weights of the precipitates produced in estimating the acidulous radicals, should correspond, within the limits of experimental error, with the sum of the numbers similarly calculated from the determination of the bases.

This concordance is not to be expected in the results from the insoluble portion, inasmuch as the silica exists in the water uncombined with any base. As also by continued evaporation the silicic acid may decompose a portion of the carbonates, the above method of verification is not applicable. The sum total obtained by division of the quantities found in estimating the acids should, however, exceed that of the bases by a number somewhat less than that calculated for the silicic acid.

In calculating out the results of the analysis of the insoluble portion, a number is substituted in the fifth column for that of the carbonic acid in the third column, of such magnitude as to render the sum of the values corresponding to the acids, less that of the silicic acid, equal to the sum found for the bases.

For calculating the results of the analysis of the soluble portion, let ABC . . . be the equivalents of acid, column III, Table D, and A₁ B₁ C₁ . . . the equivalents of base in the same column, S the sum of the former, and S₁ of the latter, then if $\frac{e}{a}$ be the probable error of such determination we have—

$$\begin{aligned} & a(1 + \frac{e}{a}) + b(1 + \frac{e}{a}) + c(1 + \frac{e}{a}) + \dots \\ &= a_1(1 - \frac{e}{a}) + b_1(1 - \frac{e}{a}) + c_1(1 - \frac{e}{a}) + \dots \end{aligned}$$

consequently—

$$\frac{e}{a} = \frac{S_1 - S}{S_1 + S}.$$

By the aid of the value of $\frac{e}{a}$ so obtained, are found the numbers in column V of the following table D, which are employed for calculating the quantities of the various salts present in the water.

In a table given by Bunsen, in the pamphlet previously mentioned, all the various salts found in mineral waters are arranged in the order of their decreasing solubility, and consequently in the order in which they would be deposited upon evaporation of a water holding all in solution.

In the soluble portion of the mineral water, the acids and bases are grouped in all the possible combinations, and the most difficultly soluble salt thus found is first estimated. In the present instance there are three acids and five bases, theoretically capable of combining to form 15 different salts. Of these the least soluble is calcium sulphate, and

$$0.000401 \times 68.04(\frac{1}{2}\text{CaSO}_4) = 0.027284 \text{ gram,}$$

represents the amount of this salt in 10,000 parts of water.

The next in order of solubility is potassium sulphate:—

$$0.001018 \times 87.19(\frac{1}{2}\text{K}_2\text{SO}_4) = 0.088759 \text{ gram,}$$

and therefore, is the amount of this salt present.

The equivalent of sulphuric acid still available—

$$0.003114 - (0.000401 + 0.001018) = 0.001695,$$

is not sufficient to unite with the whole of the sodium to form the salt next in order of solubility, hence

$$0.001695 \times 71.09(\frac{1}{2}\text{Na}_2\text{SO}_4) = 0.1205 \text{ gram,}$$

represents the amount of sodium sulphate.

In a similar manner the remainder of the constituents are calculated.

The composition of the dissolved gases being, according to the mean of the results given in the first part of this paper,

N 59.78 per cent. by volume.

CO₂ 40.22 „ „

the amount of nitrogen present has been calculated from that of the free carbonic acid, found in this analysis, by aid of this proportion.

The final result is tabulated in the usual form:—

	Parts in 10,000 of water.
Calcium bicarbonate	2·0014
Magnesium „	0·8587
Ferrous „	0·0044
Manganous „	0·0040
Barium sulphate	0·0069
Calcium „	0·0373
Potassium „	0·0888
Sodium „	0·1205
Lead „	0·0006
Sodium nitrate	0·0037
Calcium fluoride	0·0028
Sodium chloride	0·4412
Ammonium „	0·0003
Magnesium „	0·1361
Silicic acid	0·1356
Lithium	trace
Strontium	trace
Phosphoric acid	trace
Organic matter	0·0033
Free carbon dioxide	0·0287
Nitrogen	0·0272
	<hr/>
	3·9015

To facilitate comparison, the various analyses of this water which have been published have been calculated into parts in 10,000, and as the different chemists have combined the acids and bases in varying manners, the total amounts of each basylous and acidulous radical are given.

	Dr. Pearson. 1784.	Sir C. Scudamore and Mr. Garden. 1819.	Dr. Playfair. 1852.	Dr. Muspratt. 1860.	Hegner. 1876.	Thresh. 1881.
Temperature...	82° F.	—	82° F.	—	—	81·7° F.
Sp. gr.	—	—	1·0003	—	—	0·99992
Total solids ...	2·809	2·857	2·940	2·633	3·019	2·934
Ca	0·940	0·826	0·542	0·565	0·562	0·567
Ba	—	—	—	—	—	0·004
Sr	—	—	—	—	—	trace
Mg	—	0·027	0·190	0·169	0·193	0·195
Na	0·131	0·179	0·136	0·135	0·263	0·213
K	—	—	0·187	0·019	0·043	0·040
Li	—	—	—	—	trace	trace
NH ₄	—	—	—	—	0·0006	0·0001
Al	—	—	Al ₂ O ₃ } 0·034	—	—	trace
Fe	—	—	Fe ₂ O ₃ }	0·006	0·003	0·002
Mn	—	—	—	—	0·0005	0·0014
Pb	—	—	—	—	—	trace
CO ₂	1·200	1·189	1·130	1·120	1·273	1·238
Fl	—	—	trace	trace	—	0·0014
Cl	0·202	0·361	0·392	0·388	0·392	0·370
I	—	—	—	—	trace	—
SO ₄	0·336	0·080	0·234	0·033	0·142	0·160
NO ₃	—	—	—	trace	0·028	0·003
Organic matter.	—	0·095	—	0·049	—	0·003
Loss	—	0·099	—	—	—	—
SiO ₂	—	—	0·095	0·149	0·120	0·136
PO ₄	—	—	trace	trace	trace	trace*

*Gaseous Constituents in Cubic Centimetres per Litre at 0° C. and
760 mm. Pressure.*

CO ₂	} 70·0	{ 7·2 22·3	12·5	12·6	Not deter- mined.	14·56
N			743·7	1819·5		22·13

The differences observable in these analyses show that the waters examined varied considerably. Thus, whilst in 1819 the sulphates correspond to 0·080, and in 1860 to only 0·033, Playfair, in 1852, found 0·234; Hegner, in 1876, 0·142, and the present analysis gives 0·160. The quantity of potassium salts has varied to even a greater extent. The water examined by Muspratt contained less saline matter than any sample previously or afterwards examined.

These differences are perhaps not surprising, considering the number of springs supplying the thermal water. Thus, Dr. Short, writing

* Besides the above, the following elements were detected in the sinter :—

Molybdenum, copper, cobalt, and zinc.

in the year 1734, mentions "all those four springs together (St. Ann's Well, Bingham's Well, and those of the inner and outer bath), . . . the strong spring rising up in the middle of the bath level beyond St. Ann's Well, and the warm water which rises up in the Cold Spring, and lastly, the two small warm springs which rise up in the low ground between the hot and cold spring in the sough, with several other oozings of warm water in sundry other places. . . ." All these springs are now built over, and contribute to supply the various baths and pumps, and it is exceedingly probable that the composition of all is not the same. The temperature, however, of such as I have access to has not varied, but undoubtedly free gas is more abundantly evolved in some places than others.

The source from which Pearson, and Scudamore and Garden obtained the water they examined I do not find stated. Dr. Playfair appears to have collected his at the mouth of the spring at the side of the Natural bath; the source of Muspratt's is unknown to me. Hehner's, and the sample last examined, were taken from the bath. Playfair's analysis represents, therefore, the composition of one of the principal springs; Hehner's and my own, the mixed waters of all the springs flowing into the Natural bath and the reservoirs connected therewith.

Pearson estimated the dissolved gases at one-fourteenth the volume of the water, and discovered that most of it was nitrogen. Scudamore and Garden found much less free carbonic acid than has since been observed. The free nitrogen seems to be constant in amount, being 22.3 c.c. per litre in 1819, a result agreeing almost exactly with that now obtained. The cause of Playfair's and Muspratt's error has already been pointed out, and as they did not determine the nitrogen directly, their results are useless for comparison.

XXI.—*Dibenzoylaniline and its Isomerides.*

By A. HIGGIN.

By the action of benzoyl chloride upon monobenzylaniline Gerhardt is known to have obtained a dibenzoylaniline crystallising in needles, and melting at 136°. By the action of benzoic acid upon phenyl thiocarbimide at 130—150° Losanitch also obtained (*Berl. Ber.*, 1873, 176) a phenyldibenzoylamide crystallising in plates melting at 155°.

At the instance of Prof. Merz I undertook, while at Zürich, an investigation of this subject. In the repetition of the first-named

method I heated 18 grams of phenylbenzoylamide with 14 grams of benzoyl chloride at 230° in a flask attached to an upright condenser. At the expiration of three hours, the evolution of HCl having ceased, the mass was boiled with solution of sodium carbonate, and the residue treated with alcohol. From the alcoholic solution I obtained colourless needles melting at 136° . Heated in a sealed tube with dilute hydrochloric acid at 120° for four hours, the substance was completely decomposed into benzoic acid and aniline, by which result its constitution is established. Moreover it yielded on combustion 79.6 per cent. carbon (calculated for phenyldibenzoylamide 79.73); Gerhardt's results therefore are fully established. I next repeated Losanitch's work, heating 13 grams benzoic acid and 6 grams phenyl thiocarbimide at 220° for six hours in a flask as before (not in sealed tubes as recommended by Losanitch). The mass being further treated as above described, I obtained colourless plates melting at 160° . The products of resolution by dilute hydrochloric acid were as before, aniline and benzoic acid. I am therefore able to confirm the statements of Losanitch.

I may observe that it is necessary to guard against using the phenyl-thiocarbimide in excess. In an experiment in which this condition obtained, the product was a substance crystallising in needles melting at 145° , having the properties of a base, and containing sulphur. My next endeavour was to prepare an isomeride in which one of the benzoyl-groups should enter the aromatic nucleus. For this purpose I employed benzoyl chloride and phenylbenzoylamide in the ratio and under the conditions given for my first experiment, but with the addition of a few grams of zinc chloride. By subsequent treatment of the product of the reaction as before, I isolated a body crystallising in colourless plates melting at 150° . The combustion of this product gave the following percentages:—

		Calc. $C_6H_4(C_7H_5O).NH(C_7H_5O)$.
C	79.27	79.70
H	5.51	4.98

That the constitution of this body is that of a phenylbenzoylbenzoylamide is proved by the results of its decomposition by dilute hydrochloric acid in the ordinary way, the products being benzoic acid and a solid base, which separated out on addition of potash to the liquid contents of the tubes. Recrystallised from alcohol it formed opaque white needles melting at 123° . The following are the results of its combustion:—

0.237 gram yielded 0.125 H_2O and 0.688 CO_2 .

		Calc. $C_6H_4(C_7H_5O)NH_2$.
C	79.16	79.18
H	5.82	5.58

No further proof is needed that this body is a benzoylphenylamine. It yields extremely characteristic salts. The sulphate crystallised in plates, and yielded on analysis the following results:—

	Per cent.		
	(1.)	(2.)	Calc. $(C_{13}H_{11}ON)_2SO_4$
SO ₄	19.68	19.61	19.67

The hydrochloride formed a crystalline magma. On analysis—

0.3945 gram gave 0.2306 AgCl.

	Calc. $C_{13}H_{10}ON.HCl$
Cl	15.2

It also gave a crystalline platinochloride, which gave on ignition 24.38 per cent. Pt (calc. 24.48).

On concentrating the alcoholic solution from which the phenylbenzoylbenzoylamide had crystallised, I obtained in small quantity a body crystallising in rhomboïdal plates and melting at 170°. On heating with dilute hydrochloric acid at 120°, it was resolved into benzoic acid and a solid base melting at 103°. This body was therefore an isomeric phenylbenzoylbenzoylamide.

In conclusion I would briefly express my thanks to Profs. Merz and Weith for their kind advice and assistance in carrying out the above work.

XXII.—Contributions to our Knowledge of the Composition of Alloys and Metal-work, for the most part Ancient.

By WALTER FLIGHT, D.Sc., F.G.S., of the Department of Mineralogy, British Museum; Examiner in Chemistry and Physics, Royal Military Academy.

I. Facts Relating to the History of Copper-nickel Coinage.

IN 1868 I sent a short paper to the *Numismatic Chronicle** on the composition of the flat round white coins of certain kings of Bactria. I had made a quantitative analysis of a coin of Euthydemus, weighing 5.266 grams, and with a slightly longer diameter of 25 mm. The

* *The Numismatic Chronicle*, 8, 305; *Pogg. Ann.*, 139, 507; Roscoe and Schorlemmer's *Chemistry*, 2, Metals, Part II, 147.

metal of the coin was of a bright white with a very faint tinge of yellow, and exhibited, when broken, a fine granular structure of a dull grey colour, resembling that of cast steel. The analysis showed the coin to contain of copper 77·585 per cent., nickel 20·038 per cent., cobalt 0·544 per cent., iron 1·048 per cent., besides traces of other metals. The coin belonged to Major-General Cunningham, late of the Bombay Engineers, now Surveyor-General of the Archæological Survey of India. Later on I examined qualitatively several more Bactrian coins, belonging to my friend, and I found the coins of—

Pantaleon	246 B.C.
Agathokles.....	235 „
Euthydemus	235 „

to possess the same composition. Those of Euthydemus bear an image of the king on the obverse, and the representation of a very elegant tripod on the reverse, together with the king's name in Greek characters; the coins of Agathokles have the head on the obverse and a figure of a leopard on the reverse, as well as the king's name in Greek. It was fully established by this examination that one coin of Pantaleon, two of Agathokles, and two of Euthydemus, have the chemical composition already indicated. The coin was subsequently examined by Dr. Percy and M. Dumas; Dr. Percy found 20·20 per cent. of nickel and cobalt, and the results of M. Dumas' analysis have never reached me.

An idea has been put forth that these nickel pieces are forgeries; but I agree with Mr. Thomas, F.R.S., in thinking that numismatists may trust General Cunningham's perception of true and false coins, even if intractable nickel would not have been the last metal selected for manipulation. Mr. Thomas is of opinion that these coins were intended to pass at the same rate as the silver money of identical stamp. As regards value, he writes, we have the evidence of Scripture for "fine copper, precious as gold" (Ezra viii, 25, 27), and Josephus's parallel testimony for "copper more precious than gold" (vii, 53, and xi, 5). And Strabo bears witness more directly to local values in "drinking-cups and lavers of Indian copper, most of which were set with precious stones" (xv, i, 69). Apollonius, of Tyana, on his arrival at the Cophen River, observed that "the Indian money was of orichalcum and bronze—purely Indian, and not stamped like the Roman and Median coins." Mr. Priaulx, in a note, adds, "the Indian money is *ῥηκεκομψευμένη*, metal *refined*, prepared; and the Roman *κεχαραγμένη*, *stamped*. The *orichalcum* may possibly refer to the nickel pieces, the copper to the imperfectly preserved square pieces which the Bactrian Greeks left in such multitudes on these old sites." Mr. Masson remarks, "I suppose that no less than 30,000 coins, probably a much

larger number, are found annually on the *dasht* or plain of Beghrām." (*Journ. Asiatic Soc. Bengal*, 1834, 154; Prinsep's *Essays*, i, 81.)

In his elaborate paper on the "Coins of Alexander's Successors in the East," and the part "On the Monetary System of the Greeks of Bactriana, Ariana, and India,"* General Cunningham inclines to the opinion that the copper-nickel alloy must have come from China. Quintus Curtius, however, he points out, mentions that, near the junction of the Five Panjāb Rivers, Alexander received from the Oxydracæ and Malli, a present of 100 talents of "white iron" (*ferri candidi*).† He concludes that this was certainly not tin, which is a soft metal, and was besides very well known to the Greeks. But as nickel is both hard and magnetic, as well as white, it might be justly described as *white iron*. In the Greek Anthology also he finds mention of an "Indian brass as white as silver," by the poet Krinagoras, who was a contemporary of Strabo,

Χάλκειον ἀργύρεω με πανείκειλον, Ἰνδικὸν ἔργον,
 "Ὀλπην, ἡδίστου ξείνιου εἰς ἐτάρου,
 "Ἢμαρ, ἐπεὶ τὸ δε σείν γενίθλιον, διὰ Σίμωνος,
 Πίμπει γηθομένην σὺν φρονὶ Κριναγόρης.

which he translates as follows:—

This drinking-cup of Indian brass,
 As silver white, Krinagoras,
 To Simon's son, his best of friends,
 A loving birth-day present sends.

He thinks it possible that the names of "white iron" and "white or silvery brass," like that of "white copper," may refer to one of the Chinese alloys of nickel. Commerce has always been active between India and China, and it was very easy for a merchant to reach the Panjāb and Kabul from the western coast of India. One of the Buddhist legends, in fact, refers to the shipwreck of Kāka-Prabhāsan, a "merchant of Taxila," on the east coast of India.

At what value these nickel coins passed current can only be conjectured; but it seems probable that they may have been *oboli*, and, writes General Cunningham, I notice that the three nickel-striking kings have no silver *oboli*, while on the contrary, their contemporary, Antimachus I, as well as their successors, Demetrius and Eukratides, all have silver *oboli*, and no nickel coins. The one would therefore appear to have been intended as a substitute for the other; but the nickel coins soon fell into disuse, either from some inconvenience, or from the difficulty of procuring a sufficient supply of the metal. No trace of nickel has yet been discovered in any of the purely Indian coinages.

* *The Numismatic Chronicle*, 1873 [3], 13, N.S., No. li, 187.

† *Vit. Alexand.*, 9, 8.

With the view to determine how many coins of like quality were preserved in the Department of Coins and Medals in the British Museum, I inspected the collection very carefully, and I found of—

Agathokles	246 B.C.*	Two coins,
Pantaleon.....	246 „	One coin,
Euthydemus.....	225 „	Five coins,
Eukratides	200 „	None,
Philoxenes	190 (?) B.C.	One coin,
Apollodotus	168 B.C.	Five coins,
Zoilus	150—146 B.C.	One coin,

all of which, as far as I could judge simply by appearance, are formed of the copper-nickel alloy. A forgery of a coin of Eukratides was examined, and proved to be composed of silver and some copper; and a Scythian coin of Carmania, which it was thought by Mr. Thomas might consist of copper and nickel, was found to contain copper and silver only.

Nickel, as is well known, was discovered in 1751 by Cronstedt; and it was about twenty years ago that the Belgians were the first to issue a coinage of copper-nickel. I found it to contain—

Copper	74.40
Nickel	25.55
	<hr/>
	99.95

Later on the alloy was employed for coinage in North America, Peru, Switzerland, Brazil, and Honduras. In 1869 the late Master of the Mint issued a coinage of the same kind for the Island of Jamaica, in penny and halfpenny pieces, and very handsome coins they are. My friend, Prof. Graham, informed me that they contain 20 per cent. of nickel and 80 per cent. of copper; and he assured me that he should have advocated the issuing of a coinage of the same kind in the British Isles, if only a sufficient supply of nickel could at all times be obtained. Later on, about 1873, the Prussians issued five and ten pfennig pieces, and the composition of one of the pieces I found to be:

Copper.....	75.15
Nickel.....	24.94
	<hr/>
	100.09

It should, perhaps, be stated that the density of the Bactrian coin

* These dates vary somewhat from those previously given, but are the dates held by the Coin Room authorities to be correct.

was found to be 8·89, that of nickel being 8·82, and that of copper being 8·93.

II. *Coins of Ancient India.* 500 B.C.

Some curious coins of white metal, most of them square, with one corner often snipt off, others more or less rounded, and all with a design on one side only, were brought to me for examination by W. G. Lettsom, Esq. The design was of the rudest character: an elephant very roughly portrayed being common, with occasional representations of a wheel, and what appeared to be a shield with a spear crossing it. A large find of them had taken place at Chappa, near Belaspoor; and of this locality I am informed: "The name you have taken down is quite correct, Belaspoor (Belasore is in Lower Bengal), but you will not find it on any map, as the place has only within the last eight years (this was written about 1870) been made a separate district. The locally celebrated place, the capital of the old 'Hae Hae Bunsee' Rajpoot Dynasty is 'Ruttunpoor,' which you will find on most maps. It is only 15 miles from Belaspoor, and had to be abandoned on account of its fearful unhealthiness. The coins were found on the lands of a small 'Zumeendaree' or chiefship called Chappa, in the district of Belaspoor, and the Chutteesgurh Division of the Central Province. The Mahanudda is the main river of the Division, running through portions of all three of its districts Chappa itself is not 30 miles from it."

The coins analysed were found to contain:—

Silver	89·120
Silver chloride.....	1·328
Gold	1·253
Copper	4·337
Lead	3·735
Graphite	0·075
	<hr/>
	99·848

These coins are met with over a very large area of more than 2,000 miles in width, in Kabul, the Delta of the Ganges, in Southern India, Nepaul, &c. The native assayers make the percentage of silver which they contain to vary between 73 and 86; the English assayers find from 75 to 83 per cent.

III. *Figure of Buddha, Ancient India.*

About the time that Major-General Cunningham showed me the Bactrian coins to which I have referred above, he brought me a small

metallic figure, the composition of which it was thought might prove of interest. It was a figure of Buddha, much worn and smoothed, about $1\frac{1}{4}$ inch in height, with a small loop-hole over the head; the right hand is apparently raised in the act of blessing. The density of the figure was found to be 8.479, and the composition—

Silver.....	57.701
Silver chloride.....	4.113
Copper	37.548
Gold	0.483
Graphite	0.403

100.248

In most of the specimens here described, the silver, when present, was accompanied by silver chloride in varying quantities, which gives the metal the brittle character already pointed out by Mr. Church.

IV. *Bidrai Ware, India.*

Some years ago I had occasion to examine some specimens of the beautiful and well-known Indian ware, called Bidrai ware. The surface of the boxes or bottles, or bowls or flasks, is made very smooth and true, and the design, which is partly to cover it, is then cut in the surface, or rather slightly undercut. Plates of silver about the thickness of ordinary writing paper, which accurately fit these slight depressions of the surface, are then let in and pressed hard into them. They adhere to the undercut metal, and the two metallic surfaces present a fine contrast, whether the surface is polished brightly or allowed to tarnish. Although the undercutting is done with great exactness, the boxes, &c., are, as a rule, very clumsily made. The metal composing the vessel was analysed in two cases: I. A box covered with small plates of silver, from John Henderson, Esq.; and II, a bottle, with label: "Beder Work, near Secunderabad in the Deccan, Nizans Territory; from Procter & Co."

	I.	II.
Zinc (by difference)....	[94.552]	[93.516]
Copper	3.920	3.278
Lead	1.400	2.171
Gold	—	0.690
Iron	0.128	0.345
	<hr/> 100.000	<hr/> 100.000

V. *Koft Gari Work, India.*

This beautiful form of metal work is made at Goojrat and Sealkole in the Panjâb bordering Cashmere. The groundwork consists of iron plate which has been made blue by heating. The gold design overlying it appears to be painted on with a solution, reduced and burnished. The silver is laid on exceedingly thin in a sort of bar-like structure, the thicker border of the plate rivetted on to the back part with firmly adhering silver. On the back of the plate is a design drawn on with a lac, which is not acted upon by absolute alcohol.

VI. *Sickle found by Belzoni under the Feet of a Sphinx at Karnak, Egypt. Preserved in the Department of Oriental Antiquities, British Museum.*

A fragment of this iron, which is supposed to be one of the very oldest pieces of worked iron in existence, was handed to me for examination. It was of a dark-brown colour, was very friable, and slightly magnetic. On boiling it for hours with mercury chloride, it was found that no iron was removed, and the fragments remained intact. It was then treated with *aqua regia*, but no effervescence was remarked, and gold sodium chloride, and the small quantity of reduced gold removed with the silica. The gold corresponded to 1.586 per cent. of iron monoxide, which with 3.525 of iron sesquioxide indicated the presence of 5.111 per cent. of magnetite. The iron was very carefully examined by the lead method for nickel, and the precipitate of iron sesquioxide amounting to 0.2029 was found to contain rather less than a milligramme of nickel oxide. The composition of the so-called iron was found to be—

Silica.....	11.884	—
Magnetite.....	5.111	—
Calcium carbonate ..	0.172	—
Iron sesquioxide	64.604	19.38
Water (by difference)	18.229	16.20
Nickel	trace	—
	<hr/>	
	100.000	

The water appears to be present not as limonite, but as the ochre gelbeisenstein or xanthosiderite, $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

The nickel was present as a trace only, and not in sufficient quantity to allow of our regarding the metal as of meteoric origin. We shall speak on this subject further on.

VII. *Iron found in one of the Air-passages of the Great Pyramid, by Colonel Howard Vyse, in 1837.*

A fragment of this very early piece of manufactured iron, which is

preserved in the Department of Oriental Antiquities, was given me for examination by my friend Dr. Birch. Experiments made by Mr. St. John V. Day by drilling the metal had already shown that it was iron and not steel.

The results of my examination of this fragment of iron (No. 3453) from the air-passage of the Great Pyramid went to show that *it is not of meteoric origin*. It contains, it is true, a trace of nickel, but it is only a trace. It is, in fact, by no means an uncommon occurrence for a trace of that metal to be met with in manufactured iron derived from its various ores, and several analysts have detected the presence of nickel oxide in the ores likewise.

According to Pattison (*Brit. Assoc. Report*, 1864, 49), the Cleveland ironstone contains in 1 lb. of ore 0.72 grain of nickel and 0.12 grain of cobalt. O. L. Erdmann (*Jour. pr. Chem.*, 97, 120) states that he has many times found traces of cobalt (the *alter ipse* of nickel and constant associate of nickel in meteoric iron) in iron ores, and still more frequently in samples of commercial iron. It should be stated, by the way, that the presence of a trace of cobalt is more readily recognised than the same amount of nickel would be. C. O. Braun (*Zeits. Anal. Chem.*, 5, 226) mentions the fact that in many analyses of iron which have been carried out in the Wiesbaden Laboratory, the presence of nickel and cobalt has been recognised. G. Lippert (*Zeits. Anal. Chem.*, 2, 41) found in the spiegeleisen obtained from the spathic iron ore near Musen, 0.016 per cent. of nickel and a trace of cobalt.

The fragment of Egyptian iron above referred to contains combined carbon, an occurrence of the greatest rarity in meteoric iron. The locksmith who removed it from the specimen, which appears, by the way, to have been a scraper, tells me that under the saw it behaved like wrought-iron, and I find its magnetic character to accord with wrought-iron rather than with steel.

VIII. *Double Hook of "Bronze," found in another Air-passage, one of those called "Dixon's Passages," of the Great Pyramid, by Mr. John Dixon, August, 1872.*

Colonel Vyse found the air-passages of the King's Chamber in the Great Pyramid in 1837; in 1872 Mr. Dixon searched for similar channels or passages in the Queen's Chamber and found them. He drilled a hole through the upper part of the second stone from the floor about midway between the east and west wells, and at a depth of five inches a cavity was found, which disclosed a channel 9 inches by 8, which extended in a horizontal direction for the length of 7 feet, and then ascended at an angle of 32°. The other side of the chamber

was then drilled into, and a precisely similar channel met with. No trace of any outlet or opening to either channel could be discovered on the exterior of the Pyramid, and apparently there is no communication between the air-passages of the King's Chamber and those of the Queen's Chamber. At the bottom of the ascending channel on the south side, the one first found, Mr. Dixon found a small heap of *débris*, in which was the bronze hook above referred to.

The hook is shaped like an Y, and appeared to be composed of bronze, and is covered with a fine patina. It is probable that it was placed where it was found at the time that the Pyramid was built. The two hooks are flattened, and the shank carries two rivets bearing traces of ivory, probably of hippopotamus tusk. It is not improbable that this hook may have formed the upper part of the handle of a dagger. A drawing of it will be found in *Nature*, December 26th, 1872. The composition of the metal was found to be—

Copper	99·521
Iron	0·479
	<hr/>
	100·000

It consisted therefore of nearly pure copper. Von Bibra gives analyses of weapons from Siberia and Ireland that consist of a nearly pure copper. (See his "*Katolog of Bronze Legirungen.*")

IX. "*Bronze*" Figures, brought from Egypt by Mr. John Dixon.

One of the figures sent to me by Mr. Dixon was a figure of Isis; it was 8 inches in height, and declared by Dr. Birch to be of Ptolemaic time. The interior of the figure consisted of a black mould round which the figure had been cast. All the particles of this bronze were taken up by the magnet. The composition of this "bronze" was found to be—

Copper	68·421
Iron	4·694
Lead	22·759
Nickel (cobalt)	0·782
Tin.....	0·938
Arsenic.....	1·479
Antimony.....	0·668
	<hr/>
	99·741

Maumené (*Compt. rend.*, 80, 1875) found 5·68 per cent. of lead in some Japanese alloys; Kalischer as much as from 11 to 12 per cent. in some of them (*Dingl. polyt. J.*, 215); and Morin in certain specimens

from China and Japan from 9·9 to 20·31 per cent. of lead, as well as some tin (*Ann. Chim. Phys.*, 1875 [5], 3). The percentage of lead in this specimen, while below that met with in some Roman coins, hooks, and buckles, exceeds, I believe, that found in any Egyptian alloy the examination of which has yet been made.

Another bronze figure which I received from him was remarkable for its exceeding thinness, the thickness of the metal being estimated at $\frac{1}{32}$ nd of an inch, or perhaps $\frac{1}{30}$ th of an inch. It was a half-length figure, with a pointed beard and folded arms, and appears to be a singularly fluid alloy admirably adapted for casting. The interior is filled with a core of black sand, and the composition of the bronze was found to be—

Copper	82·19
Lead	15·79
Tin	2·02
	<hr/>
	100·00

Both these bronzes are distinguished by the singularly small amount of tin present in them, and by the large percentage of lead.

X. *Copper Spear-heads, from Cyprus, from the Cesnola Collection.*

Three spear-heads which were found in Cyprus, and formed part of the collection made by General Cesnola, were quantitatively analysed. One (I), the smallest of the three, was very flat, resembling the blade of a knife; the other two, about double the length of the above, were distinguished in that the metal composing them was much thicker along the middle line, giving strength to the implement. One of these (II) was barbed, the other (III) was not. None of them bear the rivetted pins, whereby many bronze heads were attached to the shaft. These three implements, it will be seen below, are not bronze, but consist essentially of copper.

	I.	II.	III.
Copper.....	97·226	98·398	99·470
Iron.....	1·322	0·729	0·384
Nickel.....	—	0·153	0·084
Gold.....	0·279	0·305	—
Lead	0·076	—	—
Tin	trace	—	—
Arsenic	1·348	trace	trace
Phosphorus.....	trace	trace	trace
Sulphur	—	0·305	—
	<hr/>	<hr/>	<hr/>
	100·251	99·890	99·938

XI. Copper Axe-heads, from Beth Saour, near Bethlehem, Holy Land, belonging to Mr. A. W. Franks, F.R.S.

Two axe-heads, one 5 inches long by 3 wide, the other $5\frac{1}{4}$ inches long by $1\frac{1}{2}$ inches wide, were examined. The one contained 99·557 per cent. of copper, with traces of iron and arsenic; the other 99·93 per cent. of copper, with traces of arsenic, nickel, and sulphur.

XII. Hebrew Shekel, from Rev. W. Drake.

This coin was one of a number which excited considerable interest in the numismatic world in 1874, because they were said to be forgeries. Mr. John Evans, F.R.S., wrote to the *Academy* respecting them, and I believe all doubts were set at rest. The coin weighed 14·2696, or 220·209 grains, had a density of 10·527, and contained—

Silver	97·674
Gold	0·676
Copper	0·642
Graphite	0·034
	<hr/>
	99·026

but no chloride of silver. Traces of lead, iron, zinc, and sulphur were, however, met with.

XIII. Cypriote, Romano-British, Greek, and Roman Bronzes.

Several interesting bronzes were analysed, and found to have the following characters:—I. From Cyprus. This was part of a sword or dagger blade, and was obtained from General Cesnola; at the end were two rivets. II. Part of a figure of Mercury, of Romano-British times; was presented to the British Museum by Sir W. Tite, and found on the site of the Old India House, Leadenhall Street. III. Handle of vase, with two figures in relief; was purchased in Samos, and is stated to have been found in the Island of Telos; it is of about the time of Alexander the Great. IV. Roman bronze figure of a boy, holding a bunch of grapes, in the Blacas Collection in the British Museum.

The composition of these specimens of bronze were found to be—

	I.	II.	III.	IV.
Copper.....	88·771	78·355	81·764	87·158
Tin	8·508	10·018	10·901	10·724
Lead.....	1·504	9·302	5·246	2·005
Iron.....	0·476	0·715	0·153	trace
Cobalt	0·304	—	1·222	—
Nickel	trace	—	trace	—
Phosphorus....	trace	—	—	—
Silver	—	—	trace	trace
Gold.....	—	—	trace	trace
	99·563	98·390	99·286	99·887

XIV. *Incas Pin, found on Mummy at Arica, S. Peru, after Earthquake, 1868.*

This curious pin, $3\frac{3}{4}$ inches in length, has a flat head, 1 inch broad and $\frac{1}{2}$ inch wide, and was found after the earthquake of 1868, by Lieutenant Harrison, of H.M. Ship "Topaze." The shock was felt at 5 and 5.30 P.M. on the 13th August, 1868, and it opened a graveyard, supposed to be Incas, and exposed a number of mummies, gold coins, pins, &c. The composition of this pin was found to be—

Silver	82·222
Silver chloride.....	1·388
Gold	0·406
Copper	16·100
Iron	0·119
	<hr/> 100·235

XV. *Bronze Bar, from Ruins of Temple, in Bolivia; from Mr. Inwards.*

A bar of bronze was found by Mr. Inwards in a ruined temple or palace at Tiahuanaco, near La Paz, Bolivia, on the borders of Titicaca, 12,000 feet above the sea-level. It is $28\frac{3}{4}$ inches long, and has a rectangular section, being in the middle 1 inch by $\frac{3}{4}$ of an inch, and slightly tapering to the ends. It is covered with a fine patina. It is difficult to say for what purpose it was constructed. The composition was found to be—

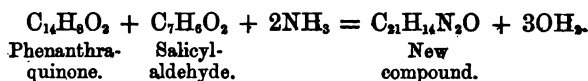
Copper	93·26
Tin	6·52
Iron.....	0·26
Nickel	trace
Arsenic	trace
	<hr/> 100·04

XXIII.—On the Action of Aldehydes on Phenanthraquinone in Presence of Ammonia. (Third Notice.)

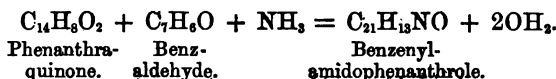
By FRANCIS R. JAPP, M.A., Ph.D., Assistant Professor of Chemistry in the Normal School of Science, South Kensington, and FREDK. W. STREATFIELD.

2. Action of Hydroxyaldehydes.

IN a former communication (*Chem. Soc. J., Trans.*, 1881, 228), by one of us, in conjunction with Mr. Wilcock, it was mentioned that by the action of salicylaldehyde and ammonia on phenanthraquinone, a compound of the formula $C_{21}H_{14}N_2O$ was obtained according to the equation—



The compound thus formed contained two atoms of nitrogen in the molecule, instead of one, as in the case of the compounds which are formed by the action of non-hydroxylated aldehydes and ammonia upon phenanthraquinone. Thus, in the case of benzaldehyde—



The present paper is devoted to an account of the results obtained with hydroxyaldehydes, and with a methoxyaldehyde, upon phenanthraquinone in presence of ammonia.

a. Action of Salicylaldehyde.

The operation was performed as in the reaction with benzaldehyde (*loc. cit.*, 225). 50 grams of finely-powdered phenanthraquinone were thoroughly mixed in a flask with somewhat more than 1 molecular proportion of salicylaldehyde and an excess of concentrated aqueous ammonia. When heated on a water-bath, the pasty mass fused, then became thick again, and ultimately solidified. During the process of heating, the flask was shaken from time to time until solidification set in. The entire reaction was completed in the course of a few minutes. The brown solid cake was powdered, boiled first with water and then with alcohol, which removed a considerable quantity of colouring matter, and was finally dissolved in boiling amyl alcohol, and the solution decolorised with animal charcoal. From this solution the substance

was deposited on cooling, in tufts of silky needles. After two or three crystallisations it was quite white, and to all appearance pure. It fused, with blackening and decomposition, about 270—276°. Analysis of the substance dried at 140° yielded numbers in which the percentage of carbon was somewhat lower than that required by the formula $C_{21}H_{14}N_2O$. We afterwards found that the substance, on heating with caustic potash, gave off a strong odour of amyl alcohol; so it was evident that, in spite of the high temperature employed in drying, a portion of the solvent had been obstinately retained by the substance. The compound was therefore recrystallised from acetic acid. It had not altered in appearance, but now gave analytical results agreeing well with the theory:—

	Substance.	CO_2 .	OH_2 .
I	0.1094	0.3258	0.0456
II	0.1130	0.3366	0.0472

III. 0.0158 gram, burnt with copper oxide in a vacuum, gave 1.15 c.c. (calibrated volume) dry nitrogen, at 18.5° and under 795.3 mm. pressure, corresponding to 0.001415 gram nitrogen.

	Calculated for $C_{21}H_{14}N_2O$.		Found.			Mean.
	I.	II.	I.	II.	III.	
C_{21}	252	81.29	81.21	81.23	—	81.22
H_{14}	14	4.52	4.63	4.63	—	4.63
N_2	28	9.03	—	—	8.95	8.95
O	16	5.16	—	—	—	(5.20)
	310	100.00	—	—	—	100.00

Properties.—Crystallises in tufts of very fine white needles, but after pressing and drying appears to the unaided eye amorphous. Fuses, with blackening and decomposition, at about 270—276°. Alcohol and light petroleum dissolve it slightly on boiling; benzene and carbon disulphide somewhat more readily. The best solvents are glacial acetic acid and amyl alcohol, from hot solutions of which it is deposited on cooling in the tufts of needles just described. It is also very soluble in ether. When boiled with moderately concentrated caustic alkalis, it first fuses to an oil under the liquid, and afterwards solidifies; on employing sufficient liquid, the whole goes into solution as an alkaline salt of the compound. From the alkaline solution, carbonic anhydride and acids precipitate the substance unchanged. Besides thus behaving like a phenol, it seems to possess the properties of a weak base; the addition of a few drops of concentrated

hydrochloric acid to the ethereal solution precipitates the whole of the substance, but the hydrochloride cannot be isolated, and the substance is insoluble in aqueous hydrochloric acid at ordinary temperatures. Concentrated sulphuric acid dissolves it in the cold, yielding a dirty violet solution with a greenish-blue fluorescence.

By fusion with potash, and by boiling for several days with alcoholic potash, salicylic acid was obtained from the substance, and was identified by the ferric chloride test. Various unsuccessful attempts were made to obtain the salicylic acid in quantity sufficient for identification by other means. The substance forms with the fused potash a salt, which is not attacked until a temperature is reached at which total decomposition ensues. Milk of lime in sealed tubes at 200° is without action upon the substance.

Concentrated hydrochloric acid was without action at 150° ; when heated to 200° , the substance dissolved and crystallised in needles on cooling; at still higher temperatures decomposition took place, but nothing definite could be isolated beyond ammoniac chloride.

We also tried to eliminate the oxygen of the substance by means of reducing agents. Distillation of 4 grams with zinc-dust in a current of hydrogen yielded only a minute quantity of a tarry distillate. Hydriodic acid and amorphous phosphorus at lower temperatures were without action; at 200° a substance with basic properties was obtained, but in quantity too small for investigation, the greater part of the original substance being resinised.

A number of attempts were made to prepare an acetyl-derivative, but neither acetic anhydride—either alone, or with sodic acetate, or with zinc chloride—nor acetyl chloride, had any action upon the substance, though the temperature was raised as high as was possible without total decomposition of the reagent.

Benzoyl-derivative.—Eight grams of the compound were heated in a large boiling-tube with about an equal weight of benzoic anhydride. The temperature was not determined, but was probably a little higher than the boiling point of benzoic acid. The fused mass boiled at first, and benzoic acid collected in the upper part of the tube; afterwards it became pasty, and ceased boiling, upon which the operation was interrupted. The cooled mass was powdered, and extracted several times with small quantities of hot alcohol, in order to remove benzoic anhydride and benzoic acid. A grey pulverulent substance remained, which was dissolved in hot benzene. On cooling, it was deposited in crystals, and after two or three crystallisations, fused constantly at $218-220^{\circ}$. The substance crystallises in two forms—small crystals, apparently cubical, and tufts of needles. Both forms have the same fusing point, and pass readily into each other.

The substance gave on analysis the following results:—

	Substance.	CO ₂ .	OH ₂ .
I	0.1480	0.4385	0.0598

II. 0.0548 gram, burnt in a vacuum with copper oxide, gave 3.93 c.c. (calibrated vol.) dry nitrogen at 20.2°, and under 635.1 mm. pressure, corresponding to 0.00647 gram nitrogen.

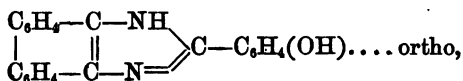
III. 0.0506 gram gave 3.93 c.c. (calibrated vol.) dry nitrogen at 16.1°, and under 585.0 mm. pressure, corresponding to 0.00358 gram nitrogen.

These numbers lead to the formula of a monobenzoyl-derivative, C₂₁H₁₃(C₇H₅O)N₂O:—

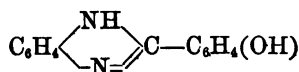
	Calculated for C ₂₁ H ₁₃ (C ₇ H ₅ O)N ₂ O.		Found.			Mean.
			I.	II.	III.	
C ₂₈	336	81.16	80.80	—	—	80.80
H ₁₈	18	4.35	4.48	—	—	4.48
N ₂	28	6.76	—	7.00	7.08	7.04
O ₂	32	7.73	—	—	—	(7.68)
	414	100.00	—	—	—	100.00

Only the value for nitrogen is decisive in showing whether a monobenzoyl or a dibenzoyl derivative has been formed, or indeed, whether a benzoyl-derivative has been formed at all, as the percentage both for carbon and for hydrogen in these two derivatives and in the original substance differs only very slightly.

Constitution of the Compound C₂₁H₁₃N₂O.—Taking into account the behaviour of this compound in forming with caustic alkalis salts decomposable by carbonic anhydride; the existence of a monobenzoyl-derivative; the preparation from it of phenanthraquinone and salicylic acid; and lastly, its mode of formation; we are led to the adoption of the constitutional formula—



as the best expression of the reactions of this compound. The substance would thus belong to the class of the *anhydro-bases* described by Hübner, and would be the exact analogue in the phenanthrene series of the compound *anhydrosalicyldiamidobenzene*—



(Hübner and Mensching, *Ber.*, 13, 463; *Annalen*, 210, 345), which was obtained by the reduction of salicylorthonitrilide. Adopting

the same system of nomenclature, the present compound would receive the name *anhydrosalicyldiamidophenanthrene*.

The constitutional formula above suggested is, however, open to some objections. The compound of Hübner and Mensching is a base, and forms well characterised salts; in the compound here described, the basic properties are almost obliterated, and this could scarcely have been predicted from the mere substitution of phenanthrylene for phenylene, though a lowering of the basic power might have been expected. Again, the behaviour of the compound towards phosphorus pentachloride and towards acetyl chloride, and its resistance to the action of so powerful a reducing agent as hydriodic acid, scarcely suggest the presence of a hydroxyl-group. (The benzoyl-group might of course equally well replace amidic or imidic hydrogen.) But all the constitutional formulæ in which the hydrogen of the hydroxyl-group in salicyl is represented as replaced by some group of atoms—for example, by the introduction of a closed chain uniting the two ortho-points of the salicyl-group—have still less probability than the above. Further, we have obtained from orthomethoxybenzaldehyde a corresponding compound, and in this case the reaction admits only of the above interpretation. From this methoxy-compound we have obtained the salicyl-compound by replacing methyl by hydrogen.

As it seemed desirable to ascertain whether the anomalous result obtained in the reaction with salicylaldehyde—the introduction of two atoms of nitrogen instead of one, into the molecule of the compound, was due merely to the presence of a hydroxyl-group in the aldehyde, or to the position of this hydroxyl-group in the molecule, it was resolved to extend the reaction to an isomeric hydroxylaldehyde, and also to a methoxyaldehyde.

b. Action of Parahydroxybenzaldehyde.

The parahydroxybenzaldehyde employed was a beautifully crystallised specimen fusing at 115–116°. The operation was conducted as in the case of salicylaldehyde, and the proportions employed were: 15 grams of the aldehyde to 27 grams of the quinone, with an excess of concentrated aqueous ammonia. The reaction took place exactly in the same manner as in the former case. The crude substance was treated with a warm dilute solution of caustic soda, in which it dissolves readily, any unaltered phenanthraquinone being left behind, and was then precipitated from the filtered solution by carbonic anhydride.

The precipitate was dissolved in hot acetic acid, decolorised by boiling with animal charcoal, and allowed to crystallise. After recryst-

tallising three or four times from the same solvent, the substance was obtained pure in the form of fine white needles. It did not fuse within the range of the mercurial thermometer, but began to blacken about 300°. Analysis gave the following results:—

	Substance.	CO ₂ .	OH ₂ .
I	0.1303	0.3874	0.0550
II	0.1894	0.5635	0.0810

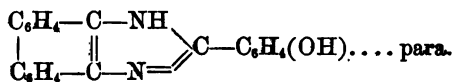
III. 0.0602 gram, burnt in a vacuum with copper oxide, gave 5.96 c.c. (calibrated vol.) dry nitrogen at 19.6°, and under 594.7 mm. pressure, corresponding to 0.00547 gram nitrogen.

These numbers lead to the formula C₃₁H₁₄N₂O—

	Calculated for C ₃₁ H ₁₄ N ₂ O.		Found.			Mean.
			I.	II.	III.	
C ₃₁	252	81.29	81.08	81.14	—	81.11
H ₁₄	14	4.52	4.69	4.75	—	4.74
N ₂	28	9.03	—	—	9.07	9.07
O	16	5.16	—	—	—	(5.08)
	310	100.00	—	—	—	100.00

(We found in this case also that the compound, when crystallised from amyl alcohol, gave somewhat too low a percentage of carbon.)

The reaction had therefore taken place exactly as in the case of the ortho-aldehyde, and we will therefore name the compound *anhydro-parahydroxybenzoyldiamidophenanthrene*, attributing to it the constitution—



Properties.—Fine white needles, fusing, with decomposition and blackening, above 350°. Soluble in hot glacial acetic acid and amyl alcohol; nearly insoluble in the other ordinary organic solvents, even at their boiling points. Dissolves readily in dilute caustic alkalis, and is precipitated from this solution by carbonic anhydride. Gives no colour reaction with concentrated sulphuric acid.

As in the case of the salicyl-compound, various attempts were made here also to replace the hydroxyl-group by hydrogen. Hydriodic acid and amorphous phosphorus seemed to have as little action upon it as upon the ortho-compound, only a small quantity of a basic substance, similar to that obtained in the former case, being produced, when the heating was continued for several hours at 200°. A distillation with zinc-dust, in which 1 gram of the compound was em-

ployed, gave a relatively good yield of an oil which solidified when treated with hydrochloric acid, and again liquefied on the addition of potash solution. We intend to repeat this distillation experiment as soon as we have succeeded in preparing a sufficient quantity of the anhydro-compound.

In contradistinction to the ortho-compound it readily forms an acetyl-derivative when treated with acetic anhydride.

Acetyl-derivative.—A portion of the substance was heated in a sealed tube with acetic anhydride at 150° for seven hours. The contents of the tube were digested for some time in the cold with alcohol, and the liquid was then poured from the crystals, which, after pressing and drying, were dissolved in boiling amyl alcohol. The substance required protracted boiling in order to bring it into solution, and separated rapidly in minute needles from the liquid while still hot. After two or three crystallisations, it fused at $205\text{--}210^{\circ}$. The fusing point could not be determined with accuracy as the substance blackened and shrunk together several degrees below its fusing point. The specimen analysed retained a slight greyish tinge, which could not be removed by crystallisation, and the smallness of the quantity of the substance at our disposal precluded the employment of other means of purification. Analysis showed that a monacetyl-derivative had been formed:—

	Substance.	CO ₂ .	OH ₂ .
I	0.1612	0.4624	0.0674

II. 0.0619 gram, burnt in a vacuum with copper oxide, gave 3.93 c.c. (calibrated vol.) dry nitrogen at 17° and under 765.8 mm. pressure, corresponding to 0.00468 gram nitrogen.

	Calculated for C ₂₁ H ₁₃ (C ₂ H ₃ O)N ₂ O.		Found.	
			I.	II.
C ₂₃	276	78.41	78.23	—
H ₁₆	16	4.54	4.64	—
N ₂	28	7.96	—	7.55
O ₂	32	9.09	—	—
	352	100.00	—	—

The acetyl-compound is very soluble in glacial acetic acid, but does not crystallise readily from the solution.

3. Action of Orthomethoxybenzaldehyde.

This aldehyde was prepared by the method described by Perkin (*Chem. Soc. J.*, 1867, 418), by heating the sodium-compound of salicyl-

aldehyde with methyl iodide in alcoholic solution. The product boiled between 230° and 233° (uncorr.).

In this reaction, in order to insure as good a yield as possible, the substances were heated to 100° in sealed tubes. 15 grams of the aldehyde and 30 grams of phenanthraquinone, together with an excess of concentrated aqueous ammonia, were thus heated for one hour. There was no pressure in the tubes on opening. The crude substance was pulverised under water, washed, dried, dissolved in hot benzene, and decolorised by boiling with animal charcoal. The benzene solution on standing deposited small compact crystals, which, when recrystallised from the same solvent, were deposited by more rapid crystallisation in yellow needles fusing constantly at $207-208.5^{\circ}$. A further quantity of this substance was obtained by concentrating the original benzene solution. The yellow colour seems to be peculiar to the substance, and not due to an impurity, as it could not be removed or even diminished by further purification. The original mother-liquor from the yellow crystals yielded a second substance crystallising in white needles. These, after recrystallising several times from hot benzene, fused constantly at $144.5-145.5^{\circ}$. They were then recrystallised from glacial acetic acid, but the fusing point remained unchanged. The yellow compound was formed in rather the larger quantity, but the relative proportions of the two products seemed to vary in different experiments.

The yellow compound yielded the following analytical results:—

	Substance.	CO ₂ .	OH ₂ .
I	0.1702	0.5078	0.0770
II	0.1308	0.3916	0.0596

III. 0.0640 gram, burnt in a vacuum with copper oxide, gave 5.96 c.c. (calibrated vol.) dry nitrogen at 11.8° and under 585.7 mm. pressure, corresponding to 0.00553 gram nitrogen.

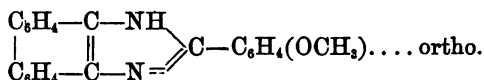
IV. 0.0857 gram, burnt in a vacuum with copper oxide, gave 7.99 c.c. (calibrated vol.) dry nitrogen at 15.8° and under 584.2 mm. pressure, corresponding to 0.00729 gram nitrogen.

These numbers lead to the formula $C_{22}H_{16}N_2O$:—

	Calculated for		Found.				Mean.
	$C_{22}H_{16}N_2O$.		I.	II.	III.	IV.	
C ₂₂	264	81.48	81.36	81.65	—	—	81.50
H ₁₆	16	4.94	5.02	5.06	—	—	5.04
N ₂	28	8.64	—	—	8.64	8.51	8.57
O	16	4.94	—	—	—	—	(4.89)
	324	100.00	—	—	—	—	100.00

M 2

The compound has therefore been formed in a reaction similar to that which takes place in the case of the hydroxyaldehydes. Two molecules of ammonia have taken part in the reaction. The compound is to be regarded as *anhydro-orthomethoxybenzoyldiamidophenanthrene*,



Properties.—Bright yellow needles, fusing at 207—208·5°. Readily soluble in boiling benzene, amyl alcohol, and glacial acetic acid: much less soluble in the cold. Insoluble in dilute acids and in caustic alkalis. Dissolves in cold concentrated sulphuric acid with a blue colour.

A portion of the substance was heated in a sealed tube with concentrated hydrochloric acid. Below 200° no action took place, except that the substance partly dissolved in the acid and crystallised out on cooling. After heating for some hours at 200°, there was a strong pressure in the tube on opening: the escaping gas burnt with a greenish flame (methyl chloride), and the tube was filled with colourless needles, which, by their fusing point, behaviour towards a solution of caustic potash, and the colour-reaction with sulphuric acid, were identified as anhydrosalicyldiamidophenanthrene, which had thus been formed by the substitution of hydrogen for methyl in the yellow compound. This reaction, as we have already pointed out, leaves no room for doubt as to the constitution of the salicyl-compound.

In the case of the white compound fusing at 144·5—145·5° the following results were obtained on analysis:—

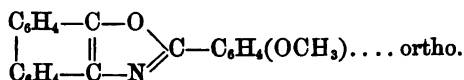
	Substance.	CO ₂ .	OH ₂ .
I	0·1141	0·3400	0·0489
II	0·0972	0·2888	0·0414

III. 0·0548 gram, burnt with copper oxide in a vacuum, gave 2·90 c.c. (calibrated vol.) dry nitrogen at 15·7° and under 561·9 mm. pressure, corresponding to 0·00255 gram nitrogen.

These figures lead to the formula C₂₂H₁₅NO₂:—

	Calculated for		Found.			Mean.
	C ₂₂ H ₁₅ NO ₂ .		I.	II.	III.	
C ₂₂	264	81·23	81·26	81·03	—	81·15
H ₁₅	15	4·62	4·76	4·73	—	4·75
N	14	4·31	—	—	4·64	4·64
O ₂	32	9·84	—	—	—	(9·46)
	325	100·00	—	—	—	100·00

The reaction in this case is similar to that which occurs with benzaldehyde and other non-hydroxylated aldehydes. Only one molecule of ammonia takes part in the reaction. The compound is therefore *orthomethoxybenzenylamidophenanthrole*—



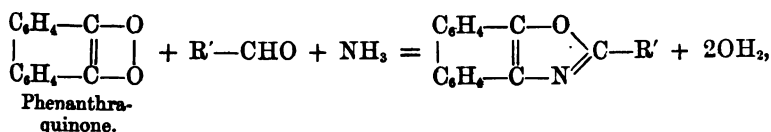
Properties.—White needles, fusing at 144.5–145.5°. Readily soluble in hot benzene, amyl alcohol, and glacial acetic acid; much less soluble in the cold; is less rapidly deposited from its solutions than the yellow compound; insoluble in dilute acids and in caustic alkalis; dissolves in cold concentrated sulphuric acid, with a greenish colour.

Summary.

The general results obtained in the investigation of the action of aldehydes upon phenanthraquinone in presence of ammonia, as contained in this and former communications, may be summed up as follows:—

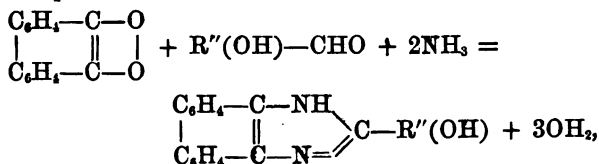
The reaction varies with the nature of the aldehyde employed.

1. With aldehydes of the benzene series the reaction takes place according to the equation—



in which R' represents a monad radicle of the phenyl series. Ordinary fatty aldehydes cannot be employed in this reaction; but furfuraldehyde, in accordance with its general chemical behaviour, acts like an aldehyde of the benzene series. The compounds formed belong to the class of substances which Ladenburg obtained (*Ber.*, 9, 1524) by the action of anhydrides or chlorides of monobasic acids upon orthoamidophenol, and in which a triad radicle of the form R'—C≡ replaces the three atoms of hydrogen in the amidogen- and hydroxyl-groups of the amidophenol.

2. When hydroxyaldehydes of the benzene series are employed, the reaction takes place as follows:—



the compound formed belonging to the class of the anhydro-bases described by Hübner. It seems in this reaction as if the presence of the electronegative hydroxyl-group in the aldehyde attracted a larger quantity of the electropositive ammonia, causing it to take part in the formation of the new molecule.

3. With a methoxyaldehyde (the behaviour of the methyl ether of salicylaldehyde has alone been studied), both the above reactions take place simultaneously, and a mixture of the two compounds belonging to the two classes is obtained, the one compound differing from the other only by the substitution of the imidogen-group for oxygen. The methoxyl-group probably stands, as regards its electrochemical properties, intermediate between hydrogen and hydroxyl; and as a fact, the reaction of the methoxyaldehyde is a combination of the reactions of the ordinary aldehyde and the hydroxyaldehyde.

In conclusion, it may be pointed out that the above reactions, which may be regarded as condensations in the ortho-series, are most readily accounted for on the assumption that phenanthraquinone possesses the peroxide constitution ascribed to it by Graebe, as expressed in the above formula (see also *Chem. Soc. J., Trans.*, 1880, 410).

One of us is at present engaged, in conjunction with Mr. H. H. Robinson, in studying the action of ammoniac formate upon phenanthraquinone. It was thought that the formic acid might play the part of an aldehyde. As the reaction, however, differs in some respects from those here described, it will form the subject of a future communication.

We have also found that phenanthraquinone, acetone, and ammonia react with great readiness upon each other at ordinary temperatures, evolving heat and forming a crystalline compound. Since in the aldehyde reactions described in the present paper, the hydrogen of the aldehydic group CHO is eliminated, the reaction with acetone must possess an essentially different character. We are at present investigating the subject, and intend also to examine the action of other ketones in this respect.

XXIV.—*Application of the Aldehyde and Ammonia Reaction in Determining the Constitution of Quinones.*

By FRANCIS R. JAPP, M.A., Ph.D., and FREDK. W. STREATFEILD.

In a previous communication (*Chem. Soc. J.*, 1880, Trans., 672) it was pointed out that the above reaction probably belongs to the class of "condensations in the ortho-series," and that consequently it ought not to be capable of extension to para-quinones. Further experiment has confirmed this view. Both benzoquinone and α -naphthaquinone yield with benzaldehyde and aqueous ammonia nothing but the brown resinous products which are formed by the action of ammonia alone upon these quinones.

As the peculiar atomic grouping which must be assumed to exist in the compounds obtained in this reaction has never been known to occur except in the ortho-series, it seemed likely that the formation of these compounds might be employed as a proof of the ortho-position in quinones. Chrysoquinone and β -naphthaquinone suggested themselves as substances suitable for investigation by this reaction.

Three grams of chrysoquinone, purified by means of the double compound with hydrogen sodium sulphite, were heated in a sealed tube with an excess of benzaldehyde and aqueous ammonia at 100° for one hour. There was no pressure in the tube on opening. The contents, which were of a pale-brown colour, and had fused together, were boiled with alcohol, and the insoluble portion dissolved in hot benzene. The benzene solution deposited on cooling silky needles, which, after recrystallising twice from the same solvent, fused between 259 — 265° . The fusing point cannot be determined with great accuracy, as the substance has a tendency to creep up the sides of the capillary tube when partially melted. The crystallised substance had a very faint yellow tinge, but was obtained white by sublimation. Analysis of the crystallised substance yielded the following results:—

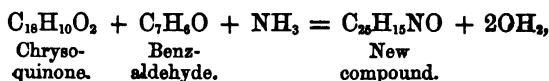
	Substance.	CO ₂ .	OH ₂ .
I	0.1128	0.3598	0.0450
II	0.1121	0.3564	0.0456

III. 0.0598 gram, burnt in a vacuum with copper oxide, gave 2.90 c.c. (calibrated vol.) dry nitrogen at 12° and under 551.7 mm. pressure, corresponding to 0.00253 gram nitrogen.

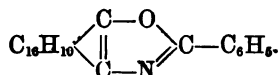
These numbers correspond to the formula $C_{25}H_{15}NO$.

	Calculated for		Found.			Mean.
	$C_{25}H_{15}NO$.		I.	II.	III.	
C_{25}	300	86.96	86.99	86.70	—	86.89
H_{15}	15	4.35	4.43	4.51	—	4.47
N	14	4.06	—	—	4.23	4.23
O	16	4.63	—	—	—	(4.41)
	345	100.00	—	—	—	100.00

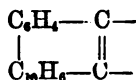
The reaction takes place according to the equation—



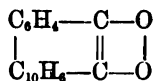
and is therefore analogous to that which occurs in the case of phenanthraquinone. The compound is the expected *benzenylamidochrysole*,



In the formula the group $C_{18}H_{10}$ is not dissected, as the question remains undecided whether the nitrogen-atom is united to a carbon-atom, which in its turn is united to the phenylene-group of chrysylenes, or to one which is united to naphthylene. The possibility of an isomerism occurring from this cause will be seen from the constitutional formula of the chrysylenes-group contained in the above compound:—



The constitution of chrysoquinone as an orthoquinone of the formula—



has been very much a foregone conclusion ever since the synthesis of chrysene from phenylnaphthylethane (Graebe and Bungener, *Ber.*, 12, 1078) and the preparation of phenylnaphthalene from chrysoquinone by heating it with soda-lime (Graebe, *ibid.*, also *Ber.*, 7, 783). The reaction now described may be taken as confirmatory of the above formula with regard to the ortho-position of the oxygen-atoms.

An experiment with β -naphthaquinone gave a negative result. A small quantity of this compound, for which we were indebted to Mr. C. E. Groves, was heated with benzaldehyde and ammonia, but yielded only a resinous mass, from which nothing definite could be extracted.

This unfavourable result was possibly due to the unstable nature of β -naphthaquinone; for, subsequently to the performance of this experiment, the ortho-position has been finally proved for this compound by P. Jacobson (*Ber.*, 14, 1794), the proof in this case also depending upon a condensation in the ortho-series.

We should be glad if chemists who are in possession of quinones of unknown constitution would test them by means of this reaction.

XXV.—*On the Action of Sodium Hydrate and Carbonate on Felspars and Wollastonite.*

By WALTER FLIGHT, D.Sc., F.G.S., of the Department of Mineralogy, British Museum; Examiner in Chemistry and Physics, Royal Military Academy.

In the qualitative analyses of rocks which contain silicates that resist the action of hydrogen chloride, as well as other silicates which are broken up by that reagent, the silicic acid of the soluble silicates remains for the most part with the silicates which are unacted upon by the acid; and it is subsequently removed by treating the entire insoluble part with sodium carbonate in which it dissolves. By some chemists the use of sodium hydrate has been recommended in conjunction with the carbonate, and even the use of the hydrate pure and simple has been suggested in place of carbonate. As the results of many analyses, more especially those of the mixed rocks which occur in meteorites, appear to contain errors arising from the use of sodium hydrate, experiments were made with the view of determining the precise nature of the action of the hydrate in each case; and a series of specimens of felspar were exposed to the action of sodium hydrate of different strengths. Each specimen was carefully picked over to obtain as pure material as possible, and was then pounded to the same extent as nearly as it could be.

A specimen of adularia from St. Gothard was dried at 120°, and digested with about $3\frac{1}{2}$ times its weight of sodium hydrate, prepared from sodium, in strong solution in a platinum vessel for 25 hours at 100°; the platinum crucible contained a little ball of platinum, which served to stir up the mixture and keep up a constant agitation. As the water slowly evaporated from the crucible it was replenished to keep it as nearly as possible at the same strength, and it was never allowed to go to dryness.

The result of the above experiment was that 35·688 per cent. of the adularia was rendered soluble; the amount of silicic acid taken up was 23·196 per cent., or of the silicate dissolved 64·996 per cent., which shows that the action of the sodium hydrate was that of a solvent only, analysis showing the adularia of St. Gothard to contain 65·69 per cent. of silica. The amount of alumina dissolved was 3·309 per cent., or one-seventh of the silicic acid, instead of between one-third and one-fourth, as it should be. The cause of this is not easily explained. That the alumina was not retained by the silicic acid was shown by evaporating it twice with ammonium fluoride, when 0·2741 gram of silicic acid was found to contain 0·0036 gram residue or 1·313 per cent.

A specimen of microclin from Siberia was next treated in the same way. Dried at 120° and carefully picked and pounded to what was believed to be the same degree, it was treated with sodium hydrate as above. There were dissolved 17·588 per cent., of which 10·946 per cent. were silica, which would make the microclin contain 62·235 per cent. of silicic acid; and 2·491 per cent. of alumina. Microclin contains from 65·5 to 65·7 per cent. of silicic acid.

A specimen of albite from the Dauphiné was dried at 120°, and treated in the same way for 22 hours, with three times its weight of solid sodium hydrate dissolved in a little water. There were dissolved 23·100 per cent., 12·553 per cent. of which was silica, and 1·466 per cent. of alumina.

These experiments were next repeated with a weaker solution of sodium hydrate. In the above experiments the amount of the solvent was three times that of the felspar; in the next set of experiments the amount of sodium hydrate was the same or, at the most, a little more than that of the powdered felspar. The conclusions arrived at in these cases were:

A quantity of adularia, another portion of the same quantity as that used above, was treated at 100° for 22 hours with a strong solution of sodium hydrate, and there were dissolved 14·693 per cent., of which 5·703 per cent. were silicic acid, and 1·752 per cent. alumina.

A quantity of the same supply of microclin, as that which was used in the above experiment, was treated for 22 hours at 100° with about its equal weight of sodium hydrate, and there dissolved 7·453 per cent., of which 4·763 per cent. were silicic acid, and 1·193 per cent. alumina.

The albite, referred to above, was in the same manner treated. A quantity was digested with about its equal weight of sodium hydrate for the usual time at 100°, and there were dissolved 9·472 per cent., of which 5·643 per cent. were silicic acid, and 2·015 per cent. of alumina.

With a view to compare the action of sodium carbonate, the

strength of the solution of which shall be such that it contains the same number of molecules as the strongest sodium hydrate previously employed on one of these feldspars, some more of the St. Gothard adularia, about 1 gram in weight, was treated with 4.56 grams of dry sodium carbonate dissolved in a very little water at 100° , for $24\frac{1}{2}$ hours, when 1.785 per cent. of the mineral was dissolved, in which were found silicic acid 0.435 per cent., and alumina 0.145 per cent.

While, therefore, the sodium hydrate acts powerfully upon these silicates as a solvent, and takes them up in large quantities, the strongest sodium carbonate has but a slight action upon them, both when the reagent is of great strength and when its action is extended over a long time.

It should, perhaps, be pointed out that in the case of the microclin three several experiments were made with a view to ascertain the proportion of the silicate which is really taken up by the sodium hydrate in each case, and it was found that when 1 gram of microclin was acted upon in each case, it led to the following analytical results:—

1 gram microclin with 0.9893 gram of sodium hydrate in strong solution for 22 hours at 100° lost 7.453 per cent., of which 4.763 per cent. were silicic acid and 1.193 per cent. alumina.

1 gram microclin with 2.894 grams of sodium hydrate, or 2.93 units in strong solution for 22 hours at 100° lost 17.588 per cent. of its weight, of which 10.946 per cent. were silicic acid and 2.491 per cent. were alumina; and in the third case

1 gram microclin with 7.704 grams of sodium hydrate, or 7.79 units, in strong solution for 22 hours at 100° lost 32.018 per cent. of its weight, of which 20.869 per cent. were silicic acid and 3.981 per cent. were alumina.

It appears from the above results as if the monoclinic feldspar was more readily acted upon by sodium hydrate than the triclinic.

At the conclusion of these experiments it seemed desirable to determine the extent to which wollastonite would be attacked under the circumstances. A specimen from Sweden was carefully picked over to separate it from a green mineral which accompanied it, and then dried at 120° , and pounded as nearly as possible to the same degree as the feldspars were. It was then digested with about three times its weight of sodium hydrate in strong solution for 22 hours at 100° , in short, under the same circumstances as those referred to in the earlier cases. There were dissolved in the soda liquid, and one containing the slightest possible excess of acetic acid, 0.5893 or 32.059 per cent. of silicic acid and lime in the ratio of 50.79 per cent. of silicic acid to 49.21 per cent. of lime, the proportion in which they occur in wollastonite; in short, the action of the reagent was that of a solvent.

XXVI.—On Pentathionic Acid. (Part II.)

By WATSON SMITH and T. TAKAMATSU.

SINCE the publication of Part I of the above research (see *Chem. Soc. J.*, 1880, Trans., 594, and *Annalen*, 207, 68), a considerable amount of work has been done and published, all of which has gone in confirmation of the conclusion arrived at as the result of our research. The conclusion was in the affirmative as regards the existence of pentathionic acid. The writings of the authors of the subsequent work above referred to, evince some misunderstanding of our methods and results in certain particulars, and this we desire to correct.

The first author, Mr. V. Lewes (*Chem. Soc. J.*, 1881, Trans., 68), proceeds at the outset of his paper to condemn any methods of proof of the existence of pentathionic acid based on analyses of the Wackenroder solution, because, he says, an acid to which he gives the formula $\text{H}_2\text{S}_6\text{O}_6$ may be present, together with tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$, exactly molecule for molecule of each of these acids. Be it remembered, however, that at the time of writing this paper, Mr. Lewes had never isolated any such acid as $\text{H}_2\text{S}_6\text{O}_6$, neither has anyone else since, much less has its existence been proved in the Wackenroder solution. Mr. Lewes' objection to our use of sulphuretted hydrogen in removing the small quantities of lead existing as lead iodide in the acid solution which we obtained in our synthetic formation of pentathionic acid, on the ground of Kessler's observation that lead tetrathionate, if present will, when decomposed by H_2S in presence of PbS , yield SO_2 , which, with H_2S , will produce pentathionic acid, would be plausible had he not overlooked the fact that on page 15, *Chem. Soc. J.*, *loc. cit.*, we mention the greater convenience which we found to follow the use of dilute sulphuric acid, in as small excess as possible, to remove lead, followed by the use of a little barium carbonate, and immediate filtration.

Spring has advanced the objection that our synthesis of pentathionic acid is only a virtual repetition of Wackenroder's method, since the action of iodine dissolved in hydriodic acid would be to set free SO_2 and H_2S , which would then react in the known manner. This we cannot allow, for in our process neither is H_2S set free, nor is S precipitated as in the Wackenroder preparation; in fact all the phenomena observed in our method point to the fact that nascent groups are split off, immediately thereafter to re-unite in a different arrangement, with considerable smoothness, which is not the case in Wackenroder's

method. Here a bulky precipitation of sulphur ensues. Hence we consider that our structural equation, given on page 13 (*Chem. Soc. J.*, August, 1880), faithfully indicates the meaning of the process.

Th. Curtius (*J. pr. Chem.* [2], 24, 225) re-investigates what he believes we intended as a complete inquiry into the precise action of the alkalis and alkaline earths upon a pentathionic acid solution. The above, however, was not our object. On this subject we commence by quoting (this Journal, 1880, Trans., 7) Stingl and Morawski's experiments and results as regards the precipitation of sulphur, more especially as *a characteristic test for pentathionic acid*. We further used magnesia as a reagent for the above purpose, preferring it to the other alkaline earths, because soluble decomposition-products would result from its use in excess (sulphites and thiosulphates) in the course of the experiment. The sulphur precipitated during the experiment would then ultimately be obtained as a pure sulphur, and not mixed with insoluble salts, as would have been the case had the other alkaline earths been employed. The success of this experiment demonstrated Spring's error, when, using barium carbonate, he obtained ultimately a precipitate which he said consisted of insoluble or sparingly soluble salts and a mere trace of sulphur; insinuating that the apparent production of precipitates of sulphur under such circumstances, had misled former observers, for these precipitates chiefly consisted of sparingly soluble salts, the sulphur accompanying them being quite insignificant in amount. This was used, together with the fact that he obtained a barium tetrathionate by the above treatment, to endeavour to prove that the Wackenroder solution contained not pentathionic acid, but only tetrathionic acid. Thus our motive in using magnesia, with which we obtained a considerable precipitation of sulphur, is explained, this motive having been misunderstood both by Curtius and by Spring.

Th. Curtius states that "Smith and Takamatsu consider the possibility of the formation of tetrathionates as excluded, in the decomposition of the pentathionic acid molecule with carbonates and hydrates of the alkalis and alkaline earths, only holding as possible that sulphites and thiosulphates are formed."

We do no such thing, however; some of the earliest results we obtained in our research showing us clearly that tetrathionates are formed, with precipitation of sulphur, on treating pentathionic acid solutions with barium carbonate. Not considering at that time that these results had any special bearing upon our principal theme, we held them over for future work. We were also perfectly aware that by partial saturation with dilute alkalis tetrathionates are formed. (See page 12, *Chem. Soc. J.*, August, 1880.)

Effect of Neutralising with Barium Carbonate a Solution of Pentathionic Acid in Dilute Alcohol.

We now proceed to give the results referred to, proving that the action of pentathionic acid upon barium carbonate, used to neutralise it, results in the formation of barium tetrathionate and free sulphur.

A weak alcoholic solution of pentathionic acid had been neutralised with freshly precipitated barium carbonate and filtered. The clear solution was then left for a long time in a dry atmosphere. A crystalline salt was thus obtained, which was collected, drained, dried, and analysed with the following results:—

Weight of salt taken	0.5570 gram.
Weight of BaSO ₄ after ignition with a drop of H ₂ SO ₄	0.3279 „

This corresponds to 34.61 per cent. Ba.

Weight of salt taken	0.4200 gram.
Weight of BaSO ₄ obtained on oxidation with HNO ₃ and KClO ₃ and precipitation with BaCl ₂ solution	0.9884 „

This corresponds to 32.33 per cent. S.

	Calculated for BaS ₄ O ₆ + H ₂ O.	Found.
Barium	34.51	34.61
Sulphur	32.24	32.33

Further, a freshly prepared quantity of pentathionic acid was mixed with a large amount of ordinary methylated alcohol. The clear solution was then neutralised with BaCO₃ and filtered. The precipitate was almost insoluble in water. It was repeatedly boiled with fresh water, the filtrates being collected. On cooling they deposited a white crystalline precipitate, which, when collected, dried over sulphuric acid, and analysed, gave the following numbers:—

Weight of salt taken	0.1485 gram.
BaSO ₄ obtained by igniting with drop of SO ₄ H ₂	0.0885 „

This corresponds to 35.04 per cent. Ba.

Weight of salt taken	0.3545 gram.
BaSO ₄ obtained on oxidising with HNO ₃ and KClO ₃ and precipitation with BaCl ₂	0.8259 „

This corresponds to 32.03 per cent. S.

	Calculated for $\text{BaS}_4\text{O}_6 + \text{H}_2\text{O}$.	Found.
Barium.....	34.51 per cent.	35.04 per cent.
Sulphur	32.24 „	32.03 „

These results were obtained when at the outset we endeavoured to obtain a barium salt of pentathionic acid. We thus proved to our own satisfaction that the attempt to neutralise pentathionic acid with alkaline earth carbonates simply results in the formation of tetrathionates, with separation of sulphur.

Effect of Excess or otherwise of Solutions of Alkalis on Pentathionic Acid Solutions.

With respect to the action of alkaline solutions, we simply referred in our paper to the action of aqueous solutions of the alkaline hydrates added *in excess*, in producing an immediate copious precipitate of sulphur (which reaction does not take place in solutions of tetrathionic acid), and hence furnishing a valuable and sharply defined line of distinction between penta- and tetra-thionic acids.

The equation we gave, $2\text{S}_4\text{O}_6\text{H}_2 + 10\text{NaOH} = 3\text{S} + 3\text{Na}_2\text{SO}_3 + 2\text{Na}_2\text{S}_2\text{O}_3$, was intended to illustrate the reaction taking place, and to this we must firmly adhere, nothing to the contrary having been proved; and it is also certain that the products of the reaction are those given in our equation.

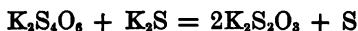
With regard to the accuracy of the equation given by Stingl and Morawski, $5\text{H}_2\text{S}_4\text{O}_6 + 10\text{HKO} = 5\text{K}_2\text{S}_4\text{O}_6 + 5\text{S} + 10\text{H}_2\text{O}$, we perfectly agree to its authority where the pentathionic acid solution is treated with an amount of dilute alkali, so as to fall far short of saturation. But we seriously dispute this authority in cases where alkalis in excess are used. In this latter case Stingl and Morawski give an equation, representing the second stage of the decomposition, as $5\text{K}_2\text{S}_4\text{O}_6 + 5\text{S} + 18\text{KOH} = 7\text{K}_2\text{S}_2\text{O}_3 + 6\text{K}_2\text{SO}_3 + \text{K}_2\text{S}_6 + 9\text{H}_2\text{O}$, and this equation we entirely dispute.

In order to put the question of the correctness of the equation of Stingl and Morawski, and our own, to a thorough re-examination, a quantity of the pentathionic acid (Wackenroder's solution) was prepared by Mr. W. H. Green, to whom we are indebted for the careful way in which he has conducted these latter special experiments for us. The strength of the acid obtained ultimately by concentration, was now determined by oxidising a known volume of it with hydrochloric acid and potassium chlorate, with subsequent precipitation with barium chloride. From this it was found that 10 c.c. of the pentathionic acid solution contained 0.668 gram sulphur = 1.077 gram $\text{H}_2\text{S}_4\text{O}_6$.

Now, pure potassium hydrate and pentathionic acid solutions were

taken in such weights as exactly to realise the proportions stated in Stingl and Morawski's equation, $5\text{H}_2\text{S}_2\text{O}_6 + 10\text{KOH} = 5\text{K}_2\text{S}_4\text{O}_6 + 5\text{S} + 10\text{H}_2\text{O}$; that is to say, 1.045 gram caustic potash and 22.3 c.c. (= 2.403 grams $\text{H}_2\text{S}_2\text{O}_6$) pentathionic acid solution, were taken. The potash was dissolved in water to form a dilute solution, which was then added to the pentathionic acid solution. A precipitate of sulphur was obtained, but by no means a copious one. On filtering a portion and testing the filtrate, *only tetrathionates* could be discovered, no thiosulphates or sulphites whatever.

On adding a further quantity of potash, so that it may be in excess, a very abundant additional precipitation of sulphur took place, and, on filtering and examining the filtrate, only sulphites and thiosulphates were discovered, but no tetrathionates. Neither in this filtrate nor in the former one were sulphides detected: hence Stingl and Morawski err in this respect. But we have already stated that potash does not decompose tetrathionic acid, and does not yield a precipitate of sulphur with it. If this be so, the question will be asked, how is it that in the further and final treatment with potash, tetrathionates are undoubtedly decomposed, only mixed sulphites and thiosulphates remaining? The solution of this problem rests on the fact that tetrathionic acid, though stable in presence of alkalis, is at once decomposed by alkaline sulphides—



(see Roscoe and Schorlemmer's *Treatise*, vol. i, p. 353).

Hence we conclude that on partial saturation of a pentathionic acid solution with an alkali, say potash, we may get a certain amount of potassium pentathionate formed, together with the realisation of Stingl and Morawski's equation, $5\text{H}_2\text{S}_2\text{O}_6 + 10\text{KOH} = 5\text{K}_2\text{S}_4\text{O}_6 + 5\text{S} + 10\text{H}_2\text{O}$. This accords with V. Lewes' experience (*Chem. Soc. J.*, 1881, *Trans.*, 71, 74, &c.). If now the opalescent solution obtained on filtering be treated with more potash, then the 5S in the above equation previously insoluble and inert (no free alkaline hydrate being present to dissolve it) is partially dissolved to form alkaline sulphides, when at once $\text{K}_2\text{S}_4\text{O}_6 + \text{K}_2\text{S} = 2\text{K}_2\text{S}_2\text{O}_3 + \text{S}$ follows, and also our equation as regards pentathionates still left behind in the fluid: $2\text{K}_2\text{S}_2\text{O}_3 + 8\text{KOH} = 3\text{S} + 3\text{K}_2\text{SO}_3 + 2\text{K}_2\text{S}_2\text{O}_3$. This fully explains the further copious precipitation of sulphur ensuing on further addition of alkaline hydrates. We cannot admit Curtius' view that with employment of excess of alkaline hydrate there is still an intermediate formation of alkaline tetrathionate: for the existence of tetrathionates is barely possible where sulphur and alkaline hydrate occur together, and quite impossible where the sulphur is in the nascent state. Doubtless, then, where the alkali is in excess, 2 atoms

of sulphur are at once split off the pentathionic acid molecule, yielding directly the groups $\text{K}.\text{SO}_2.\text{OK}$ and $\text{KS}.\text{SO}_2.\text{OK}$.

On page 12 (*Chem. Soc. J.*, 1880, Trans.) we show that when the pentathionic acid solution is shaken with ether, and the ethereal solution treated with alcohol, the whole being then treated with a little potash solution, *tetrathionate* is obtained as the decomposition-product. The action is feeble because the points of contact are diminished, as it were, through the diminished solubility of the potash in the new menstruum. Now Lewes has shown that by far undersaturating the Wackenroder solution with very dilute alkali, tetrathionates are formed, besides pentathionates, and can be crystallised out; and this agrees with a more recent observation of the action of a weak ether-alcohol solution of alkaline hydrate on pentathionic acid: for by working on a larger scale, we have succeeded, by the gradual evaporation of such a solution, in obtaining mixed crops of crystals consisting of both pentathionates and tetrathionates.

XXVII.—On Some Constituents of Resin Spirit.

By G. HARRIS MORRIS, F.C.S., Demonstrator in the Chemical Laboratories of the Mason Science College, Birmingham.

THE products of the dry distillation of resin have been made the subject of much investigation by chemists.

As early as 1835, Frémy (*Ann. Chim. Phys.* [2], 59, 13; *Ann. Chem. Pharm.*, 15, 284) investigated the products of the distillation of resin, both alone and with quicklime. In the former case he obtained water, turpentine, and a substance boiling above 250° , to which he gave the name "*resinein*," and the formula $\text{C}_{20}\text{H}_{30}\text{O}$, considering it to be directly derived from resin by the splitting off of a molecule of water. In the latter case he obtained two liquids, one "*resinon*," boiling at 78° , and having the formula $\text{C}_{11}\text{H}_{18}\text{O}$, the other, "*resineon*," boiling at 148° , and corresponding with the formula $\text{C}_{20}\text{H}_{46}\text{O}$.

In 1838 Pelletier and Walter (*Ann. Chim. Phys.* [2], 67, 267; *Pogg. Ann.*, 44, 81; *Gmelin Org. Chemie*, 4te Auflage, 3, 690) studied the products obtained from the distillation of resin in the preparation of resin gas for lighting purposes. They described a series of hydrocarbons—

Retinaphtha, C_7H_8 , b. p. 108° .

Retinyl, C_9H_{12} , b. p. 150° .

Retinol, C_8H_8 , b. p. $236\text{--}244^\circ$.

Metanaphthalin, m. p. 67° , b. p. 325° .

Thénard, Robiquet, and Dumas (*Compt. rend.*, 1838, 1, 460) confirmed these results with the exception of the last hydrocarbon, which they concluded was not isomeric with naphthalene, but had the formula $C_{26}H_{44}$, and which they named "retisteren."

Coming down to later times, Schiel (*Annalen*, 115, 96) investigated the products of the distillation. He separated the products into three divisions. First, the gaseous products, which consist of a mixture of carbonic anhydride, carbon monoxide, ethylene, propylene and diteryl (octané), and are therefore highly inflammable. These gases continue to be given off during the whole time of the distillation. Secondly, the *resin spirit*, a light, mobile, easily inflammable liquid, which boils between 97° and 250° . Schiel considers this to be a mixture of two substances, viz., "colophonon," boiling at 97° , and having the composition $C_{11}H_{18}O_2$, and a terpene boiling at 160° . And thirdly, *resin oil*, a heavy, viscid, fluorescent liquid boiling above 250° , which Schiel considered to be a mixture of several substances.

Couerbe (*J. pr. Chem.*, 18, 165; *Beilstein's Org. Chemie*, 341) has obtained a pentine from the gas obtained by the dry distillation of resin. It boils at 50° .

Resin oil and the so-called naphthalin have been examined by Curie (*Chem. News*, 30, 189; *Staedel's Jahresber.*, 1874, 453), who has prepared the hydrocarbon by distilling resin with sulphur, and has named it "colophthaline." He describes some of its derivatives which possess, according to him, remarkable properties.

Kelbe (*Ber.*, 13, 88) has obtained abietic acid in considerable quantities from the resin oil boiling above 360° .

From the resin spirit a large number of substances have been separated by various observers. Kelbe (*Ber.*, 13, 1157) describes two cymenes, boiling at 170° to 178° , one of which, metaisocymene, is new (*Annalen*, 210, 1); he also (*Ber.*, 14, 1240) found an aromatic hydrocarbon, $C_{11}H_{16}$, in the fraction boiling 190 — 200° . Isobutyric and methylpropylacetic acids have also been separated by the same chemist (*loc. cit.*, and *Ber.*, 15, 308) from the low fractions by washing with caustic soda and decomposing the resulting sodium salts.

Renard (*Compt. rend.*, 91, 419; *Ber.*, 13, 2000; *Chem. Soc. J.*, Abstr., 1880, 893) obtained a hydrocarbon having the formula C_7H_{12} , and named by him "heptene." It boils at 103 — 104° . He also describes (*Bull. Soc. Chem.*, 36, 215; *Ber.*, 14, 2583) several other hydrocarbons obtainable from resin spirit, whose boiling points range from 130° to 173° .

Tilden (*Ber.*, 13, 1604) has identified isobutylaldehyde in the lowest boiling fractions of resin spirit; he also describes a hydrocarbon boiling at 103 — 104° , and a heptane, b. p. 95 — 97° .

Mills ("Destructive Distillation," p. 31) and Anderson (*Chem. News*,

20, 76) have also studied to some extent the products of the distillation of resin.

It has long been observed that the lower fractions of resin spirit yield, on standing for some length of time, a crystalline substance, which appears more readily if the vessels containing the spirit are loosely stoppered. This body has been examined by Tichborne (*Pharm. J. Trans.* [3], 1, 302), Mills (*loc. cit.*) and Anderson (*loc. cit.*). Dr. Tilden, in his paper mentioned above, announced his intention of further studying this body. Owing, however, to pressure of work in other directions, he was unable to carry out his intention, and kindly gave the substance into my hands for investigation.

Preparation of the Substance.

The crystals are prepared by allowing the lighter portions of resin spirit to stand in large flasks containing about an equal quantity of water. The flasks are tied over with paper, thus allowing the spirit to have free contact with the air. The flasks are repeatedly shaken up, and after standing for some weeks, the watery liquid is separated from the thick oily residue, and gently evaporated on a water-bath. On allowing the concentrated solution to cool, a mass of crystals separates out, which may be purified by repeated crystallisations from water. The substance obtained in this way forms beautiful colourless crystals, often of considerable size.

When the air-dried substance is heated, it melts and gives off a quantity of water, whilst the residue forms, on cooling, a brittle white mass.

Analyses of the Crystals.

The three chemists mentioned above have each obtained different results upon analysis of this substance. Tichborne names the body obtained by crystallisation from water "colophonie hydrate," and assigns to it the formula $C_{10}H_{22}O_3 \cdot H_2O$, whilst to the dehydrated substance the name "colophonine" and the formula, $C_{10}H_{22}O_3$, are assigned.

The numbers he obtained were as follows:—

For the anhydrous substance—

	I.	II.	$C_{10}H_{22}O_3$ requires
Carbon	63.16	62.86	63.15
Hydrogen	11.10	11.72	11.58
Oxygen	—	—	25.27
			<hr/> 100.00

For the hydrated substance—

	Found.	Theory.
Carbon.....	57.35	57.70
Hydrogen	11.32	11.53
Oxygen	—	30.77
		<hr/> 100.00

He regards colophonine as isomeric with terpin hydrate, or more probably a homologue of terpin, and derived from terebene, which, however, has since been proved by Armstrong and Tilden (*Ber.*, 12, 1752) to have no existence, the liquid described as such being a mixture of camphene, cymol, and terpine.

Anderson assigns to the so-called colophonine the formula $C_7H_{14}O_3$, having obtained the following numbers upon analysis:—

For the anhydrous body—

	I.	II.	$C_7H_{14}O_3$ requires
Carbon	64.43	64.47	64.61
Hydrogen	11.09	11.24	10.77
Oxygen	—	—	24.62
			<hr/> 100.00

he regards it as being related to terebic acid, $C_7H_{10}O_4$. He did not analyse the hydrated crystals.

Mills gives—

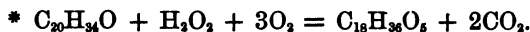
For the anhydrous substance—

Carbon	64.69
Hydrogen	11.23
Oxygen	24.08

From these numbers he obtained the formula $C_{18}H_{36}O_6$, which requires—

Carbon	65.06
Hydrogen	10.84
Oxygen	24.10

He regards the crystals as being produced from terpinol by the action of hydrogen peroxide and oxygen, thus:—



For the subjoined analyses, the hydrated substance was prepared by several crystallisations from water, and the crystallised substance was pressed between folds of blotting-paper and then dried by long exposure to the air. The dehydrated body was obtained from this by

* Tilden *Chem. Soc. J.*, 1878, 247, and 1879, 286) has since shown that terpinol has the formula $C_{10}H_{17}OH$.

repeated sublimations and removal of the water given off by bibulous paper. Finally, the substance was distilled three or four times, the last distillate fused, and the fused mass broken up and powdered. Thus obtained, it was a perfectly white powder. Burnt with oxide of copper in a closed tube, finishing in a current of oxygen, it gave the following numbers :—

- I. 0·1860 gram substance gave 0·4394 gram CO_2 , and 0·1812 gram H_2O .
 II. 0·1906 gram substance gave 0·4496 gram CO_2 , and 0·1911 gram H_2O .

	I.	II.	$\text{C}_7\text{H}_{14}\text{O}_2$ requires
Carbon	64·43	64·33	64·61
Hydrogen	10·81	11·14	10·77
Oxygen	—	—	24·62
			<hr/> 100·00

These numbers agree closely with those obtained by Anderson, as will be seen from the subjoined table.

The hydrated crystals gave the following results upon analysis :—

- I. 0·2244 gram substance gave 0·4668 gram CO_2 , and 0·2168 gram H_2O .
 II. 0·2336 gram substance gave 0·4850 gram CO_2 , and 0·2279 gram H_2O .
 III. 0·1413 gram substance gave 0·2944 gram CO_2 , and 0·1452 gram H_2O .

	I.	II.	III.	$\text{C}_7\text{H}_{14}\text{O}_2 \cdot \text{H}_2\text{O}$ requires
Carbon.....	56·73	56·62	56·82	56·75
Hydrogen....	10·75	10·82	11·42	10·81
Oxygen	—	—	—	32·43
				<hr/> 99·99

These results point to the formula $\text{C}_7\text{H}_{14}\text{O}_2$ for the anhydrous body, and $\text{C}_7\text{H}_{14}\text{O}_2 \cdot \text{H}_2\text{O}$ for the hydrated crystals. The means of the analyses obtained by the different observers are tabulated below. It will be seen that they do not differ very considerably from each other.

	Tichborne.	Mills.	Anderson.	Morris.
Hydrated crystals, C....	57·35	—	—	56·72
" " H....	11·32	—	—	10·99
Anhydrous body, C....	63·01	64·69	64·65	64·38
" " H....	11·41	11·23	11·16	10·95

The vapour-density of the anhydrous substance was taken by Hofmann's method, and gave the following result :—

Weight of substance taken	0.0682 = P
Observed volume of vapour	50.5 c.c. = V
Height of mercury column above level in trough	428 mm. = H
Height of barometer	735 mm. = B
Boiling point of aniline	190° C. = t
Temperature of room	16.5 C. = t'
Tension of mercury vapour at 190° C	15 mm. = T
Mercury column corrected to t'	= H'
Vapour-density required	= D

$$H' = H [1 - 0.00018 (t - t')],$$

$$H' = 428 [1 - 0.00018 (190 - 16.5)],$$

$$H' = 414.6 \text{ mm.}$$

$$D = \frac{P \cdot (1 + 0.00367t) \cdot 760 \cdot 14.42}{0.0012932 \cdot V(B - H' - T)} \text{ (hydrogen = 1),}$$

$$D = \frac{0.0682 (1 + 0.00367 \cdot 190) \cdot 760 \cdot 14.42}{0.0012932 \cdot 50.5 (735 - 414.6 - 15)} = 63.6.$$

	Found.	$C_7H_{14}O_2$ calculated.
Vapour-density	63.6	65

Properties of the Crystals.

This body is readily soluble in water, alcohol, ether, benzol, &c., and crystallises from its solutions in brilliant colourless prisms. When heated, it begins to sublime about 100° C., and melts at about 106°, giving off water. When the whole of the water is removed, the dehydrated substance melts at 89.5°, and boils without decomposition at 195.6° (corr.). The solution in water is perfectly neutral to test-paper, and gives no precipitate with basic lead acetate or ammoniacal silver nitrate. When the crystals are treated with sulphuric or hydrochloric acid, and warmed, a series of colours is observed in the order of yellow, red, green, deep blue; and on adding this liquid to alcohol, a magnificent green colour is communicated to it. Phosphoric, tartaric, and citric acids give the same reactions. Excess of hydrochloric acid in the cold, gives, after standing, a fine rose colour with alcohol. A very small quantity of the substance gives these reactions, so that it constitutes a delicate test for this substance, and also for the hydrocarbon to be described further on.

The hydrated crystals cannot be completely deprived of their water of crystallisation over sulphuric acid in a vacuum. A portion appears to be given off, but the substance itself is volatile, and the sulphuric acid gradually becomes green, in consequence of the reaction above mentioned.

Formation of the Crystals.

The boiling point of the fraction from which this body is obtainable in the largest quantity is variously stated. Anderson gives 125—150°, Mills 154—163°, whilst I find that the fraction boiling between 100—105° furnishes by far the largest supply, although crystals separate out from all the fractions ranging from 94—150°, after they have been standing for some time, either in loosely stoppered bottles or bottles partially filled with air.

According to Anderson (*loc. cit.*) resin spirit contains a hydrocarbon boiling at 70—80°, which he considers to be a heptylene. It gave the following percentage on analysis:—

	Found.	Calculated C_7H_{14} .
Carbon	84.62	85.7
Hydrogen.....	13.71	14.3

Vapour-density determination gave—

	Found.	Calculated C_7H_{14} .
Vapour-density....	3.257 (air = 1)	3.386

He considers the lowness of the numbers to be due to the presence of oxygen.

Renard (*Compt. rend.*, 91, 419) describes a hydrocarbon obtained from resin spirit, which he calls "heptene." It boils at 103—106°, and gave the following numbers:—

	I.	II.	C_7H_{12} requires
Carbon	87.2	87.3	87.5
Hydrogen.....	12.7	12.7	12.5

The vapour-density determination gave—

	Found.	C_7H_{12} requires
Vapour-density....	3.22 (air = 1)	3.31

It has a specific gravity of 0.8031 at 20°; it is colourless, mobile, has a characteristic odour, and is soluble in alcohol and ether. It absorbs oxygen very readily, and is without action upon an ammoniacal solution of copper chloride or silver nitrate.

It gives with bromine two compounds, $C_7H_8Br_2$ and $C_7H_{12}Br_2$. The formula of the latter was obtained by observing the amount of bromine, which a known quantity of the hydrocarbon decolorised, when the two were brought together in ethereal solution.

Oxidised with nitric acid of 1.15 sp. gr., it yields, according to Renard, carbonic anhydride, carbon monoxide, acetic, formic, oxalic, and succinic acids.

Treated with a mixture of ordinary and fuming sulphuric acid, it yields a hydrocarbon, "diheptene," $C_{14}H_{24}$, polymeric with the first, boiling at $235-250^\circ$, and giving on analysis:—

		$C_{14}H_{24}$ requires
Carbon	86.9	87.5
Hydrogen	12.2	12.5

This hydrocarbon is very oxidisable, and quickly resinifies on exposure to the air. It absorbs oxygen eight or ten times as rapidly as heptene.

Tilden (*loc. cit.*) describes a liquid from the same source, boiling steadily at $103-104^\circ$, which gave on analysis:—

	I.	II.	C_7H_{12} requires
Carbon	86.90	87.09	87.5
Hydrogen	12.39	12.57	12.5

but he considered it to be a mixture of hydrocarbons. It gives on treatment with sulphuric acid, a hydrocarbon boiling at $245-247^\circ$, and containing—

	Found.	$(C_7H_{14})_n$ requires	$(C_8H_{16})_n$ requires
Carbon	87.36	87.5	88.2
Hydrogen	12.09	12.5	11.8

This Dr. Tilden considered at the time to be a polymerised terpene; but, as will be seen from the calculated numbers, it agrees almost exactly with the percentage required for diheptene.

A vapour-density determination was made of the above-mentioned hydrocarbon by Hofmann's method. The numbers obtained were:—

Weight of substance taken	0.0470	= P
Observed volume of vapour	31.2 c.c.	= V
Height of mercury column above level in trough	612.5 mm.	= H
Height of barometer	754 mm.	= B
Boiling point of aniline	190° C.	= t
Temperature of room	15° C.	= t'
Tension of mercury vapour at 190° C. ..	15 mm.	= T
Mercury column corrected to t'		= H'
Density required		= D

$$H' = H [1 - 0.00018(t - t')],$$

$$H' = 612.5 [1 - 0.00018(190 - 15)],$$

$$H' = 593.4 \text{ mm.}$$

$$D = \frac{P \cdot (1 + 0.00367t) \cdot 760 \cdot 14.42}{0.001293 \cdot V \cdot (B - H' - T)} \text{ (hydrogen = 1).}$$

$$D = \frac{0.0470 \cdot (1 + 0.00367 \cdot 190) \cdot 760 \cdot 14.42}{0.0012932 \cdot 31.2(754 - 593.4 - 15)}$$

$$D = 94.23.$$

	Found.	(C ₇ H ₁₂) ₂	(C ₈ H ₈) ₄
Vapour-density....	94.23	96	136

The result agrees closely with that required for diheptene. The hydrocarbon used, for which I am indebted to Dr. Tilden, was boiled with sodium for some hours, and finally distilled from that metal.

From these results there can be no doubt that the hydrocarbon contained in resin spirit, and boiling at 103—104°, is a heptene.

The anhydrous substance may then be regarded as derived from this hydrocarbon by the addition of 2 semi-mols. of hydroxyl—



and the hydrated crystals as being the hydrate of this body with 1 mol. of water, C₇H₁₂(HO)₂.H₂O.

Both the hydrocarbons mentioned above give, even immediately after distillation from sodium, the series of colours referred to in connection with the crystals.

Oxidation of Heptene.

Nitric Acid.—When heptene is added to nitric acid of 1.3 sp. gr., a violent action takes place, torrents of red fumes are evolved, and the liquid shows the characteristic green colour. Upon boiling this disappears, carbonic anhydride is evolved, and, after a time, a crystalline sublimate begins to form upon the sides and neck of the flask. When the action is complete, the sublimate is washed back into the acid liquid, and the whole distilled.

The crystalline body then distils over with the volatile acids. It was collected, washed, and dried. It is soluble in alcohol, and crystallises from it in shining plates. It appears to be a *dinitro-heptylene*. The purified substance gave the following numbers on analysis:—

- I. 0.1576 gram substance gave 0.2579 gram CO₂, and 0.0925 gram H₂O.
- II. 0.1650 gram substance gave 21.7 c.c. of nitrogen at 754.2 mm. Bar., and 13° C.

	I.	II.	C ₇ H ₁₂ (NO ₂) ₂ requires
Carbon	44.62	—	44.68
Hydrogen	6.52	—	6.38
Nitrogen	—	15.44	14.89

Dinitro-heptylene is easily soluble in alcohol, ether, and benzol,

insoluble in water, and not decomposed on boiling with alkalis. It is volatile in a current of steam. It melts at 182° , and sublimes a little above that temperature, undergoing partial decomposition. I am at present endeavouring to obtain this substance in larger quantities by a different method.

The distillate containing the volatile acids was neutralised with sodium carbonate, evaporated to a small bulk, and fractionally precipitated with silver nitrate. The silver salts gave the following numbers:—

1st precipitate 0.1160 gram gave 0.0646 gram Ag.

2nd " 0.0480 " 0.0276 "

	I.	II.	Silver butyrate requires
Silver	55.68	57.50	55.38

The liquid after precipitation contained acetic and formic acids.

On evaporating off the remainder of the nitric acid on a water-bath, a crystalline acid remained. This was repeatedly evaporated with water to expel the whole of the nitric acid, and then crystallised from water. It was slightly discoloured, and gave the following numbers on analysis:—

0.1950 gram acid gave 0.2862 gram CO_2 and 0.0972 gram H_2O .

		$\text{C}_2\text{H}_4(\text{COOH})_2$ requires
Carbon	40.02	40.68
Hydrogen	5.53	5.08
Oxygen	54.45 (by diff.)	54.23

The acid gave all the reactions for succinic acid. The barium salt, which was slightly discoloured, was prepared by mixing a solution of the acid, neutralised with ammonia, with barium chloride, and then precipitating with alcohol. The air-dried salt gave the following results on analysis:—

I. 0.2511 gram salt gave 0.2189 gram BaSO_4 .

II. 0.7001 gram salt lost 0.0507 on drying at 100°C .

	I.	II.	Calculated for $\text{C}_2\text{H}_4(\text{COO})_2\text{Ba}, \text{H}_2\text{O}$.
Barium	51.24	—	50.55
Water	—	7.24	6.64

The barium salt dried at 100° gave—

0.4856 gram BaSO_4 from 0.5286 gram salt.

	Found.	$\text{C}_2\text{H}_4(\text{COO})_2\text{Ba}$.
Barium.....	54.01	54.15

The products, therefore, of the oxidation of heptene with nitric acid

are: carbonic anhydride, formic, acetic, butyric, and succinic acids. There is also formed in small quantity dinitroheptylene.

Potassium Bichromate.—Heptine, oxidised with a 10 per cent. solution of bichromate, is completely converted into carbonic anhydride and acetic acid.

The acid distillate, after oxidation, neutralised with barium carbonate, gave on evaporation a crystalline barium salt. This salt, purified by recrystallisation at a low temperature, gave the following numbers:—

I. 0.6625 gram salt gave 0.5026 gram BaSO_4 .

II. 0.8416 gram salt lost 0.1398 gram H_2O .

III. 0.7018 gram dry salt gave 0.6414 gram BaSO_4 .

	Found.	Calculated for $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$.
I. Barium	44.60	44.20
II. Water	16.61	17.40
III. Barium	53.70	$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ 53.72

Potassium Permanganate.—Heptine is readily oxidised by potassium permanganate solution, yielding an acid which has not yet been examined. No carbonate is formed.

Oxidation of the Crystals.

The crystalline substance oxidised with nitric acid of 1.3 sp. gr. yields the same acids, with the exception of formic, as the hydrocarbon.

The volatile acids, treated in the same way as the acids in the latter oxidation, gave silver salts, giving the following numbers:—

1st precipitate 0.1042 gram salt gave 0.0575 gram silver.

2nd " 0.1092 " 0.0624 "

	I.	II.	$\text{AgC}_4\text{H}_7\text{O}_2$ requires
Silver	55.18	57.14	55.38

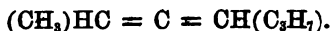
The non-volatile acid agrees in all its reactions with that obtainable from the hydrocarbon.

0.4570 gram of the barium salt gave 0.3915 gram BaSO_4 .

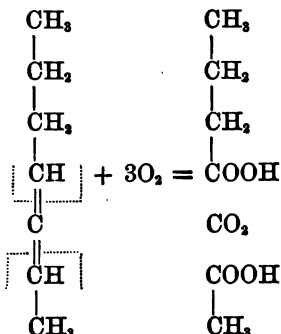
	Found.	$\text{C}_2\text{H}_4(\text{COO})_2 \cdot \text{Ba} \cdot \text{H}_2\text{O}$.
Barium.....	50.76	50.55

Probable Constitution of Heptine and its Glycol.

From the products of oxidation of the hydrocarbon, it is probably methylpropylallylene—

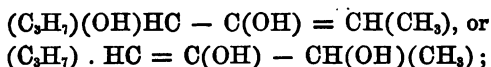


this would probably split up on oxidation, thus:—



yielding butyric and acetic acids and carbon dioxide. The succinic and formic acids may result from a secondary oxidation or from the oxidation of the butyric acid (Sigel and Belli, *Annalen*, 180, 207).

The dehydrated crystals would then have the constitution—



either of these would yield butyric and acetic acids on oxidation. It would then be methylpropylallyleneglycol.

Action of Acetic Anhydride upon Methylpropylallyleneglycol.

The substance was heated with twice its weight of acetic anhydride upon a water-bath. After a short time the liquid became dark coloured, and deepened in colour on distilling off the excess of acetic anhydride. The residue was then evaporated on a water-bath. A dark-coloured syrup was left, which on standing deposited a quantity of crystalline matter. This was drained on a filter-pump, dried between blotting-paper, and crystallised from alcohol. The acetate thus obtained crystallises in square plates, melting at 68·5°. It is very soluble in alcohol, ether, and benzol, so soluble that it was found impossible to free it, by this means, from a slight discoloration.

Warming the alcoholic solution with animal charcoal was equally unsuccessful. The acetic acid was determined by boiling a weighed quantity with caustic potash, acidifying with sulphuric acid, distilling off the acetic acid liberated, and neutralising the distillate with barium carbonate. The barium acetate was filtered off, and the solution evaporated to dryness in a weighed dish and dried at 110°.

Treated in this way—

0·3311 gram substance gave 0·4014 barium acetate.

	Found.	$C_7H_{12}(C_2H_3O_2)_2$ requires
$(C_2H_3O_2)$	56.08	55.01

The compound obtained from the crystals and acetic anhydride is therefore the diacetate.

Action of Bromine.

When bromine is added in slight excess to an aqueous solution of the crystals, a heavy yellow oil separates out. This oil is soluble in alcohol, benzene, and ether. A bromine determination of the dried oil gave the following result:—

0.3052 gram substance gave 0.5198 gram silver bromide and 0.0178 metallic silver.

	Found.	$C_7H_{12}Br_4$ requires
Bromine.....	76.70	76.92

The watery liquid from which the oil has been separated becomes almost solid, upon standing in contact with air, from separation of a black substance, which appears to be identical with that obtained by the action of sulphuric acid on the hydrocarbon or crystals.

Action of Hydriodic Acid on the Hydrocarbon.

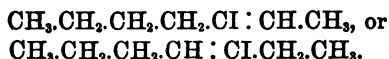
When gaseous hydriodic acid is passed into heptene it is rapidly absorbed, the liquid becomes dark coloured, and if the temperature is allowed to rise, the characteristic green colour is produced. The gas was passed into the hydrocarbon until the liquid was saturated, the temperature being kept down. The dark-coloured iodide was separated from a small quantity of resinous matter formed, washed with a little dilute caustic potash to remove free hydriodic acid and iodide, and dried with calcium chloride.

The iodide was, however, still dark coloured, resembling a solution of iodine in potassium iodide, and slowly decomposed on standing. It boiled between $140-150^\circ$, decomposing, and giving off large quantities of hydriodic acid. An iodine determination by Carius' method gave the following numbers:—

0.1854 substance gave 0.2049 AgI.

	Found.	$C_7H_{12}I$ requires
Iodine.....	59.76	56.60

It is therefore a moniodide, the high percentage found being due to the spontaneous decomposition of the substance. Assuming the hydrocarbon to be methylpropylallylene, the formula of the iodide would be—



Experiments were made in order to prepare the corresponding alcohol, but without success.

Portions were treated with potassium acetate and caustic potash, lead hydrate and water, as recommended by Flavitzky (*Annalen*, 175, 380), and moist silver oxide, but in each case a hydrocarbon was obtained boiling at 103—104°, and possessing all the properties of the original hydrocarbon.

A portion of the regenerated hydrocarbon was set aside with water, as in the preparation of the crystals; and, after some days, the watery liquid contained a considerable quantity of the crystalline body.

As already mentioned, both the hydrocarbon and the crystals give with acids and other reagents, such as bromine, chlorine, &c., a black substance soluble in spirit, producing a fine green colour. This body is at present under investigation, together with some other reactions of the bodies above mentioned.

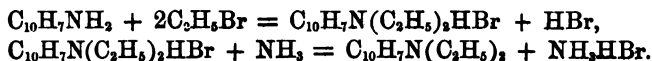
XXVIII.—On the Preparation of Diethylnaphthylamine.

By BERNARD E. SMITH.

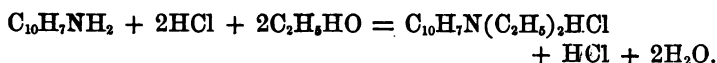
DIETHYLNAPHTHYLAMINE is best prepared by the action of ethyl bromide on naphthylamine, at a temperature of 100—120°.

I took 10 grams of naphthylamine and 15 grams of ethyl bromide, together with a small quantity of ethyl alcohol, to dissolve the naphthylamine, enclosed them in a glass tube, and heated the tube for about eight hours, at a temperature of 120°. After allowing the tube to cool, the contents were removed to an evaporating basin, the alcohol evaporated, and the residue extracted with boiling water and a little dilute hydrochloric acid. On adding ammonia to this solution, diethylnaphthylamine is precipitated, and may be obtained by shaking out with ether in a separating globe. On evaporating off the ether, the base remains behind as a dirty black oil, which can be easily purified by distillation.

The decomposition may be expressed by the following equations:—



I have also attempted to prepare diethylnaphthylamine by the action of hydrochloric acid and ethyl alcohol, instead of ethyl bromide, upon naphthylamine, thus :—



It requires, however, a much higher temperature, over 250° , and does not yield anything like so large an amount of diethylnaphthylamin.

Diethylnaphthylamine thus prepared is a pale straw-coloured oil, boiling at 290° (uncorr.), rapidly darkening on exposure to light and air. It has a slightly tarry odour and a burning taste, and burns with a lurid smoky flame. It is strongly caustic, easily forms salts with acids, and is miscible in all proportions with alcohol, ether, benzene, &c.

Analysis yielded the following results:—

		Found.			
	Calculated.	I.	II.	III.	IV.
C.....	84.42	84.18	84.25	—	—
H.....	8.54	8.78	8.97	—	—
N.....	7.04	—	—	7.25	7.33

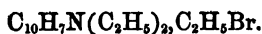
Diethylnaphthylamine hydrochloride is formed directly by the addition of hydrochloric acid to the base. It is very soluble in hot water, from which it separates on cooling, in small opaque silky plates.

The double platinum salt is easily formed by the addition of platinum chloride solution to the aqueous solution of the diethylnaphthylamine hydrochloride; after allowing the solution to stand for a short time, the salt crystallises out in golden-yellow silky plates.

Analysis yields numbers leading to the following formula:—
 $[C_{10}H_7(C_2H_5)_3HCl]_2PtCl_4$.

0·2730 gram gave Pt per cent.	24·027 }	Theory per cent. Pt.
0·1925 " 	24·049 }	24·04

In the preparation of diethylnaphthylamine I also obtained in small quantities a body which is unattacked by alkalis, and crystallises from water in small silky plates, much resembling diethylnaphthylamine hydrochloride. This body decomposes below its melting point, and yields on analysis numbers corresponding with the formula



		Found.	
	Calculated.	I.	II.
Bromine	38.45	38.14	38.31 per cent.

This compound yields diethylnaphthylamine when treated in the following manner*:—On adding a dilute aqueous solution of the substance, an excess of sulphuric acid and potassium ferrocyanide, a precipitate is formed. The base is thrown down as a salt, diethylnaphthylamine hydroferrocyanide; and on adding ammonia to a solution of this salt in water, the diethylnaphthylamine is precipitated, and may be extracted with ether.

Nitrosodiethylnaphthylamine.—I have also succeeded in preparing this substance by dissolving 5 grams of diethylnaphthylamine in glacial acetic acid, and adding to the carefully cooled solution, in small quantities at a time, a slight excess of sodic nitrite. On diluting the solution with much water, the nitrosodiethylnaphthylamine was precipitated. I then filtered and dissolved the precipitate in boiling alcohol, from which it crystallised in beautiful reddish-golden scales.

Analysis gave the following numbers:—

	Calculated.	Found.		per cent.
		I.	II.	
C	73·690	73·280	—	
H	7·018	7·129	—	"
N	12·280	12·420	12·39	"

Nitrosodiethylnaphthylamine is very soluble in ether, alcohol, and benzene. It melts at 165°, and yields a deep blue colour with sulphuric acid.

XXIX.—On the Action of Sulphuric Acid upon Diethylnaphthylamine at High Temperatures.

By BERNARD E. SMITH.

MICHLER and SALATHÉ having pointed out (*Ber.*, 14, '2161) that by the action of sulphuric acid upon dimethylaniline at a temperature of 180—200°, a tetramethylbenzidine is produced, I thought it would be interesting to see if an analogous reaction took place when diethylnaphthylamine was similarly acted upon. For this purpose I mixed together in a flask 20 grams of diethylnaphthylamine with 20 grams of sulphuric acid, and heated the mixture for about eight hours in an oil-bath at 190—210°. The mixture rapidly darkened, and water and sulphur dioxide were evolved. The reaction appeared to be completed in about seven hours. After allowing the product to remain a short time longer,

* For a similar method see *Annalen der Chemie*, 140, 184.

the flask was removed from the oil-bath and left to cool, when the contents became a thick pasty yellow mass, having a beautiful green fluorescence. On boiling with water it dissolved, with exception of a small quantity of carbonaceous matter. After filtering this off, I added barium hydrate in excess, and filtered. The residue on the filter was extracted with boiling dilute hydrochloric acid, and to the extract, after filtering off the insoluble barium sulphate, ammonia was added in excess, whereby a white flocculent precipitate was formed. This was filtered off, crystallised from alcohol, and the crystals were washed with a small quantity of ether, to remove a trace of diethylnaphthylamine. On again crystallising the body from alcohol, it was obtained in colourless tufts of needles, which, however, rapidly blackened on exposure to light and air.

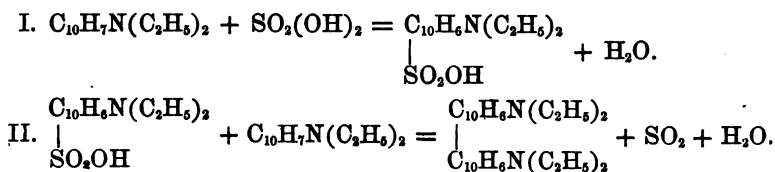
The body thus obtained melts at 190° , and may be distilled without decomposition, its boiling point, however, being much above 360° . It dissolves in hydrochloric acid, forming a red solution, from which, however, the hydrochloride crystallises in white silky plates. Its solution in strong nitric acid has an intense damson-red colour, which, however, rapidly fades to a dirty brown. It is very soluble in hot alcohol, less so in cold, not very soluble in ether, but very soluble in benzene and chloroform. It easily forms salts with acids.

Analysis yields numbers leading to the formula



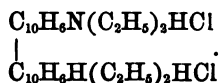
		Found.			
	Calculated.	I.	II.	III.	IV.
C.....	84.84	84.60	84.77	—	— per cent.
H.....	8.08	8.23	8.17	—	—
N.....	7.07	—	—	7.25	7.19 „

I infer that this body is the result of two different decompositions, thus:—



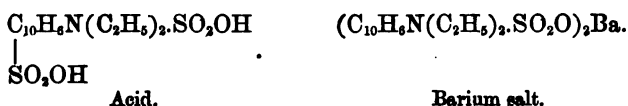
The hydrochloride is easily prepared by adding the acid to the base, and dissolving the resulting mass in boiling water; on cooling, the salt crystallises out in white silky plates.

Analysis gave numbers corresponding with the formula



	Calculated.	Found.	
		I.	II.
Cl	15.13.	15.27	15.32 per cent.

The solution from which the base had been precipitated by barium hydrate, was next examined. Carbonic anhydride gas was first passed through it, to precipitate the excess of barium hydrate. After filtering off the precipitated carbonate, the clear solution, which had a yellow colour and a beautiful bluish-green fluorescence, was evaporated down until crystals began to appear; it was then left to cool, when a mass of crystals separated out. These proved on analysis to be the barium salt of an acid having the following formula:—



Analysis of the barium salt:—

	Calculated.	Found.	
		I.	II.
Ba	19.76	19.89	19.93 per cent.

The free acid was obtained by adding sulphuric acid to the solution of the barium salt, filtering off the precipitated barium sulphate, and evaporating the clear solution down until on cooling the acid crystallised out. On recrystallisation from water, the acid was obtained in colourless flat needles.

This acid yields a salt only when heated with diethylnaphthylamine at 200°, at which temperature there was no evolution of sulphur dioxide. From this fact I am inclined to think that there are two isomeric acids produced by the action of sulphuric acid upon diethylnaphthylamine, one of which immediately reacts with a fresh molecule of the base, giving off sulphur dioxide and water, and forming the double molecule, whilst the other acid remains passive, or at least forms a salt only by joining itself to the ammonia nucleus.

I hope at some future date to have the honour of laying before the Society the results of further investigations in support of this theory.

XXX.—*On the Action of Carbon Oxydichloride (Phosgene Gas) upon Diethylnaphthylamine.*

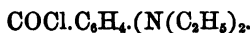
By BERNARD E. SMITH.

DIETHYLNAPHTHYLAMINE (25 grams) was dissolved in about twice its volume of carefully dried benzene, and phosgene gas passed into the solution to saturation. During the passage of the gas the contents of the flask became slightly warmed, and a white crystalline mass separated out. When fully saturated with phosgene gas, the contents of the flask were emptied out into an evaporating basin, and the benzene evaporated off over a water-bath; a black semi-solid mass remained behind. This was successively treated with boiling water and boiling dilute hydrochloric acid, the solution was filtered, and the residue washed to remove the last trace of hydrochloric acid. Both the aqueous and the hydrochloric acid solutions were found on examination to contain only diethylnaphthylamine hydrochloride.

The residue on the filter was next dissolved in alcohol. On allowing this solution to cool, and the alcohol to evaporate slowly in the air, a mass of crystals separated out, having a dirty brown colour, which, however, was easily removed by digesting with animal charcoal. By fractional distillation three distinct bodies were obtained, viz. :—

1. A colourless, transparent body, crystallising from alcohol in minute quadratic prisms, melting at 70°, and unattacked by dilute acids, or by boiling with caustic potash-solution.

Analysis yielded numbers agreeing nearly with the formula



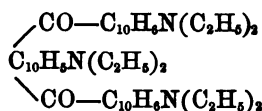
		Found.				
	Calculated.	I.	II.	III.	IV.	V.
C	68·830	68·31	68·20	—	—	—
H	6·110	6·28	6·76	—	—	—
N	5·364	—	—	5·66	5·72	—
Cl	13·570	—	—	—	—	13·82

2. A colourless crystalline body, crystallising from alcohol in transparent hexagonal prisms, melting at 225°, with decomposition, unattacked by dilute acids, or on boiling with caustic alkalis. It yields on analysis numbers corresponding with the formula of a body isomeric with that first described.

		Found.				
	Calculated.	I.	II.	III.	IV.	V.
C	68.83	68.98	69.11	—	—	—
H	6.11	6.42	6.76	—	—	—
N	5.36	—	—	5.43	5.67	—
Cl	13.57	—	—	—	—	13.73

3. A colourless crystalline body, crystallising from alcohol or glacial acetic acid in beautiful rhombs, which have a very high refractive power. This body was insoluble in water, and was not attacked by boiling with either dilute acids or alkalis.

Analysis yielded numbers corresponding with the following formula:—



		Found.			
	Calculated.	I.	II.	III.	IV.
C	81.35	81.41	81.07	—	— per cent.
H	7.24	7.53	7.39	—	— "
N	6.47	—	—	6.77	6.30 "

The melting point of this body is 130°.

One molecular proportion of each of the bodies containing chlorine was enclosed in separate tubes, with a molecular proportion of diethylnaphthylamine, and heated for about five hours at 180—200°. After cooling the tubes were opened, when a quantity of gaseous hydrochloric acid escaped. Their contents were then removed and digested with dilute hydrochloric acid and water. Nothing entered into solution except a trace of diethylnaphthylamine hydrochloride. The residue, which in each case had a deep red colour, was then dissolved in alcohol. The solution thus obtained, after boiling for a short time with animal charcoal, was left at rest, in order that the substance might crystallise out. In both cases I obtained a body corresponding in every particular with the third body, $\text{C}_{44}\text{H}_{47}\text{N}_3\text{O}_2$, obtained by the action of phosgene gas upon diethylnaphthylamine at ordinary temperature.

Analysis of body obtained by the action of diethylnaphthylamine on the body containing chlorine, melting at 70°:—

0.1244 gram yielded C	81.11 per cent.
" " H	7.39 "
0.2073 " N	6.60 "

Analysis of body resulting from the action of diethylnaphthylamine upon the body containing chlorine, melting at 225°:—

0.2102 gram yielded C 81.40 per cent.

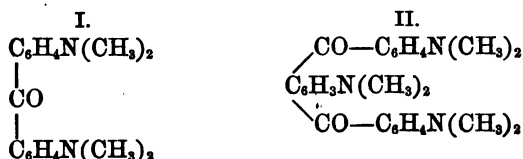
" " H 6.95 "

0.1953 " N 6.78 "

Michler (*Ber.*, 9, 400) obtained by an analogous series of reactions, in which he substituted dimethylaniline for diethylnaphthylamine:

1. A compound to which he gave the formula $\text{Cl} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2$; this body he found was easily decomposed on boiling with caustic alkalis, or even by prolonged boiling with water, thus differing essentially from either of the isomeric compounds containing chlorine obtained by me.

By heating a molecular proportion of this compound (*Ber.*, 9, 716) with a molecular proportion of dimethylaniline, he obtained two distinct bodies, to which he assigned the following formulæ:—



The second of these bodies is analogous to that obtained by me; but I have been unable, even after repeated trials, to obtain the slightest trace of a body analogous to the first, which Michler described as having high basic properties.

XXXI.—Contributions to the Chemical History of the Aromatic Derivatives of Methane.

By RAPHAEL MELDOLA.

In the year 1877, when studying the action of benzyl chloride upon diphenylamine, I observed that the viscid oily product obtained by this reaction gradually turned green on exposure to the air. Proceeding on the assumption that this colouring matter was produced by the slow oxidation of some compound formed in the reaction, I found that the oily product in question, when treated with suitable oxidising agents, yielded a large quantity of a green colouring matter which, after purification, was introduced into commerce by the firm of Brooke, Simpson, and Spiller, in whose laboratory these investigations were made, under the name of "Viridine." Specimens of the dye-stuff were exhibited in the International Exhibition at Paris in 1878,

and last year I published a preliminary note* giving an outline of the method of preparation employed. I have for some time past been continuing at intervals my investigations into the action of benzyl chloride upon diphenylamine and other monamines, and I now have the pleasure of communicating some of the results to the Chemical Society. I may state that my experiments have led to the conclusion that the crude product resulting from the action of commercial benzyl chloride upon diphenylamine is a complex mixture containing at least two distinct series of compounds, viz., derivatives of triphenylmethane and of diphenylmethane, the former being produced by certain impurities in the benzyl chloride employed.

Derivatives of Triphenylmethane.

In the first place it will be desirable to give some details as to the mode of preparation which was at first employed for manufacturing the technical product.

Diphenylamine was cohobated with a considerable excess of commercial benzyl chloride for some hours, as long as HCl was freely evolved, and the unaltered benzyl chloride was then distilled off, the thermometer rising finally to about 200° C. The oily product was transferred to an open vessel and heated in a steam-bath for about twelve hours with a mixture of a 75 per cent. solution of arsenic acid and hydrochloric acid, the whole being constantly stirred. When the maximum amount of colour was produced, the crude product was washed thoroughly with hot water in order to remove arsenic compounds and other impurities, and when cold the brittle resinous mass was powdered and washed several times with toluene. This last solvent removes a considerable amount of impurity, and the colouring matter is left as a dull bronzy powder, the hydrochloride of a new base, to which I shall again have occasion to allude further on.

In this form the colour is soluble in alcohol but insoluble in water, and experiments were therefore made with a view to form a sulphonic acid. It was found that the new green readily formed such acids when gently warmed with strong sulphuric acid on a water-bath. The alkaline salts of the lowest sulphonic acid possessed the property of dyeing woollen fabrics from an alkaline bath like the lower sulphonic acids of triphenyl-roaniline ("Nicholson blues"), this property being unique among green colouring matters at the time of its discovery.†

* *Ber.*, 14, 1385; see also the *Journal of the Society of Arts*, April 16th, 1880, p. 445.

† As already stated in the preliminary note, published last year, an "alkaline green," produced by the action of chloranil upon benzyl-diphenylamine, and the conversion of the resulting product into a sulphonic acid, has since been patented by

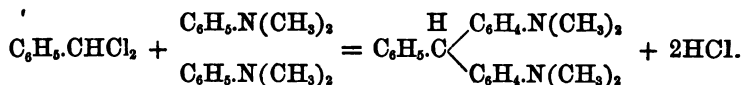
The commercial product is the sodium salt of the lowest sulphonic acid of the new base, and was exhibited in the French International Exhibition as an "alkaline-green."

The foregoing technological details will suffice to make clear the subsequent steps in the scientific examination of the product in question. For the purpose of purification, samples of the crude hydrochloride left after the toluene washing, were basified by agitation with a mixture of benzene, alcohol, and caustic soda solution. The base dissolves in this mixture with a reddish-brown colour, and, on dilution with water, the benzene solution of the base floats to the top and separates as a distinct layer. After repeated washing with water, the upper layer is drawn off and saturated with dry HCl gas, the hydrochloride being thus precipitated in the form of bronzy microscopic nodular crystals. The latter when dry were dissolved in boiling alcohol acidulated with hydrochloric acid; the solution of the colour was filtered in order to remove an insoluble tarry residue, and the filtrate diluted with about one-fourth of its bulk of aqueous hydrochloric acid. The solution when cold deposits the hydrochloride of the green base in a granular form. This treatment had to be repeated once or twice before specimens were obtained sufficiently pure for analysis.

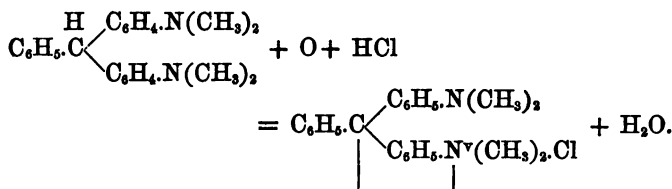
Before giving the results of the analysis, I should state that at a very early stage of my investigations, the admirable researches of Oscar Doebner and of Emil and Otto Fischer upon the condensation-products of tertiary aromatic bases, had led me to suspect that diphenylamine-green was related to the rosaniline group of colours. It was in fact a statement made by Doebner in a paper published in 1878 (*Ber.*, 11, 1237), that led me to form those theoretical views of the constitution of the new green, which were subsequently confirmed by experiment. This author found that commercial benzyl chloride contains a considerable quantity of the higher chlorinated benzal chloride ($C_6H_5.CHCl_2$) and traces of benzotrichloride ($C_6H_5.CCl_3$), so that all samples of such benzyl chloride that I have ever met with give malachite-green, often in considerable amount, when heated with dimethylaniline in the presence of zinc chloride. I was thus led to suspect that the production of diphenylamine-green was analogous to the formation of malachite-green, and this view was confirmed by experiments upon the action of benzotrichloride upon diphenylamine in the presence of $ZnCl_2$, to which reaction I shall again have occasion to refer.

Now, the researches of the authors mentioned have shown that the firm of Meister, Lucius, and Co., but I have not yet met with this colour in commerce.

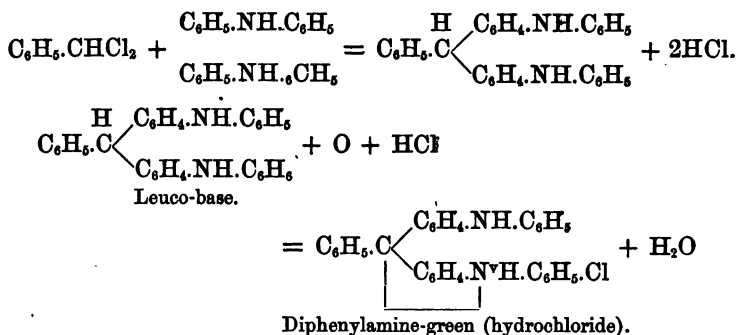
formation of malachite-green from benzal chloride and dimethylaniline is represented by the following equation:—



The leuco-base (tetramethyldiamidotriphenyl-methane) on oxidation in presence of an acid, gives a salt of malachite-green:—



On the assumption that an analogous reaction takes place in the technical operations previously described, the formation of diphenylamine-green would be thus represented:—



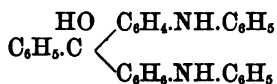
The formula thus ascribed to diphenylamine-green was confirmed by the analytical results:—

Combustions of the Hydrochloride.

- I. 0.2642 gram burnt with lead chromate gave 0.7847 gram CO_2 and 0.1332 gram H_2O .
 - II. 0.3006 gram burnt with CaO gave 0.0952 gram AgCl .
 - III. 0.1815 " " 0.0550 "
 - IV. 0.2014 " " 0.0626 "
- (I and II the same preparation, III and IV different preparations.)

	Theory for $C_{31}H_{26}N_2Cl$		Found.			
	I.	II.	III.	IV.		
C_{31}	372.0	80.78	81.00	—	—	—
H_{26}	25.0	5.42	5.60	—	—	—
N_2	28.0	6.09	—	—	—	—
Cl	35.5	7.71	—	7.83	7.49	7.68
	<hr/> 460.5	<hr/> 100.00				

Considerable difficulty was experienced in obtaining the free base in a state suitable for analysis. The hydrochloride of the green, purified by the foregoing method, was dissolved in boiling alcohol, and the solution, having been made alkaline with ammonia, which at once discharges the colour, was largely diluted with cold water and left at rest. The base then separates out as a gummy mass which solidifies only after long standing; it is readily soluble in ether, benzene, chloroform, and carbon disulphide, and is dissolved also by boiling alcohol or acetone. From none of these solvents could it be obtained in a crystalline state. Theory indicates that the formula of this base should be thus indicated:—



Combustions of Base.

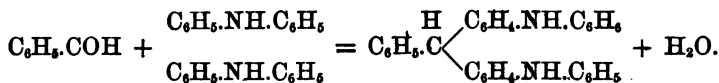
- I. 0.3735 gram burnt with CuO gave 1.1595 gram CO_2 and 0.2030 gram H_2O .
 II. 0.3245 gram burnt with CuO gave 1.0003 gram CO_2 and 0.1738 gram H_2O .
 III. 0.2239 gram burnt with CuO gave 0.6872 gram CO_2 and 0.1220 gram H_2O .

	Theory for $C_{31}H_{26}N_2O$		Found.		
	I.	II.	III.		
C_{31}	372	84.14	84.66	84.07	83.71
H_{26}	26	5.88	6.03	5.95	6.05
N_2	28	6.33	—	—	—
O	16	3.65	—	—	—
	<hr/> 442	<hr/> 100.00			

(Combustions I, II, and III were three different preparations.)

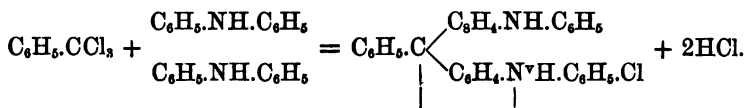
The base of diphenylamine-green is thus *diphenyldiamidotriphenylcarbinol*, and the leuco-base from which it is derived, *diphenyldiamidotriphenyl-methane*. Specimens of the latter were prepared by heating

a mixture of benzal chloride and diphenylamine with powdered zinc chloride, and also by Fischer's method, viz., by heating diphenylamine and benzaldehyde with powdered zinc chloride—



In both these processes, after the termination of the reaction, the zinc chloride was removed by boiling with water; the crude product was then washed with alcohol, and obtained in a flocculent state by dissolving it in warm aniline, and pouring the solution in a thin stream into a large bulk of alcohol. After it had been collected, thoroughly washed with alcohol, and dried, a final purification was effected by dissolving in cold ether and filtering the ethereal solution into alcohol. The leuco-base was finally obtained as a non-crystalline white granular powder, readily soluble in ether, benzene, chloroform, and carbon disulphide, and but very slightly soluble in boiling alcohol, glacial acetic acid, or acetone. Exposed to the air, it gradually turns green, and passes at once into diphenylamine-green when heated with suitable oxidising agents. When heated, the leuco-base does not become completely fused till about 170° ; but, as it softens long before this temperature is reached, no definite melting point could be determined.

It is obvious that diphenylamine-green could be obtained by other and more advantageous processes than the one at first employed in manufacturing this substance. As already mentioned, benzotrichloride was employed at a very early stage of the investigation, and a colour was obtained apparently identical with the technical product. The reaction is in this case, of course, analogous to the formation of malachite-green.

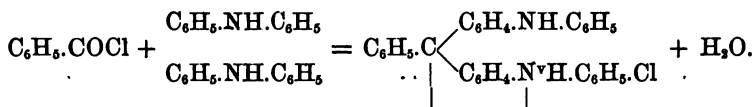


This method has quite recently been given by Doebner (*Ber.*, 15, 237), who has not, however, further examined the colouring matter. Beyond giving a few practical details, I do not propose, therefore, to enter at present any further into the scientific examination of these bodies.

In order to obtain the green by the action of benzotrichloride upon diphenylamine, the two substances are mixed together in the proportions indicated by the foregoing equation, and a quantity of anhydrous powdered zinc chloride of about half the weight of the diphenylamine employed is stirred in. The colour begins to form at once in the cold,

and the reaction is rapidly completed by gently warming the mixture on a water-bath. Doebner's statement with reference to the occurrence of benzotrichloride in commercial benzyl chloride, is fully confirmed by using diphenylamine and zinc chloride as a test reaction. Even the most carefully fractionated benzyl chloride gave a distinct green coloration under these circumstances, and diphenylamine thus serves as a most delicate test for the presence of $C_6H_5.CCl_3$. The crude product obtained by the foregoing reaction is washed with hot water in order to remove the zinc chloride, and then extracted several times with cold toluene, which leaves the hydrochloride as a dull bronzy powder. Its identity with the technical product was proved by analysis. The yield is from 70 to 80 per cent. of the theoretical quantity.

Of other methods of obtaining this colouring matter, I may mention the action of benzoyl chloride upon diphenylamine:—

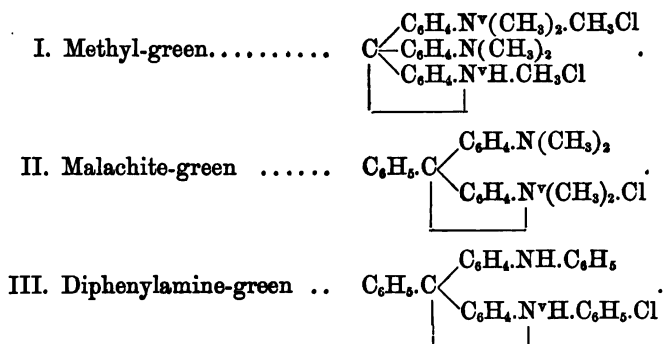
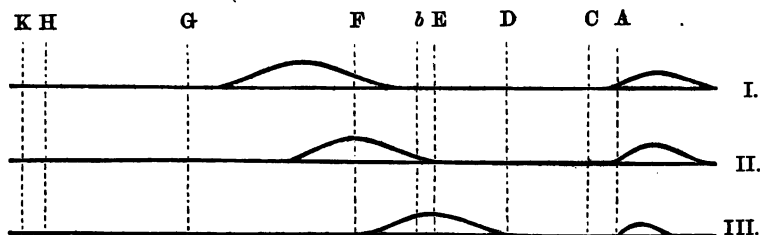


The materials are mixed and gently warmed with zinc chloride as in the previous reaction, but the yield appears to be much smaller. The colour has also been recently obtained by Doebner by heating diamido-triphenyl-carbinol with aniline hydrochloride (*Ber.*, 15, 257).

On adding a solution of platinic chloride to an alcoholic solution of the hydrochloride of the green, a dark green precipitate is thrown down, but this platinum salt is apparently that of some oxidised product of the colouring matter, as no regular results could be obtained on analysis.

Owing to their insolubility in water, the salts of diphenylamine-green cannot be conveniently made use of for dyeing purposes. By employing the alcoholic solution of any of its salts, silk and wool can be dyed of a dull bluish-green shade much inferior in brilliancy to malachite-green.

Optical Properties of Diphenylamine-green.—The dull colour of this colouring matter, as compared with the nearly related malachite-green, made it an interesting question to study the absorption spectrum in connection with those of the other green colours derived from triphenylmethane. Alcoholic solutions of the hydrochlorides of "methyl-green," "malachite-green," and the new diphenylamine-green were accordingly prepared of equal depths of colour, and their action upon a ray of light transmitted through equal lengths of the solutions observed by means of a single-prism spectroscope. The spectra are mapped in the accompanying diagram:—



[The spaces enclosed between the curves and the horizontal lines represent the amount and nature of the light *transmitted* by the solution].

The red band transmitted by diphenylamine-green is much feebler than the corresponding bands transmitted by the other greens, and I was thus led to hope that by employing a great depth of solution, the red might be completely cut off, and that great desideratum of those employed in researches upon colour, viz., an optically pure green, by this means obtained. In accordance with this idea, specimens of diphenylamine-green were forwarded to Lord Rayleigh, who was good enough to report upon the colour as follows:—"When enough is used to extinguish sufficiently the red and blue ends of the spectrum, the green is also considerably enfeebled by absorption, so that the colour, though pure, is not so brilliant as might be." The dulness of the colour thus arises from a general absorption both in the green and red, and is an inherent optical property, which cannot be due to any impurity, since the chemically pure hydrochloride was made use of for spectroscopic examination. Although the precise bearings of this fact cannot at present be perceived, I have thought it best to record it, as much work is now being done in various quarters in the most important field of the connection between the chemical constitution of bodies and their optical properties.

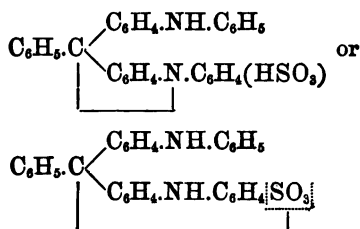
Sulphonic Acid of Diphenylamine-green.—The base of this colouring

matter, or its salts, dissolves readily in an excess of strong sulphuric acid, giving a deep brownish-red solution. By gently warming on a water-bath for a few minutes, till a drop of the solution on dilution with water gives a precipitate soluble in a boiling solution of sodium carbonate, a mono-sulphonic acid is produced. To purify the latter for analysis, the sulphuric acid solution was poured in a thin stream into cold water, and the dark green flocculent precipitate, after being collected and washed, was dissolved by boiling with sodium carbonate solution. On filtering and acidulating the filtrate, the sulphonic acid was obtained in a flocculent state, and after being collected and well washed with hot water, was dried in the water-oven and combustions made.

- I. 0.3910 gram burnt with lead chromate gave 1.0624 gram CO_2 and 0.1773 gram H_2O .
 II. 0.2631 gram deflagrated with KHO and KNO_3 gave 0.128 gram BaSO_4 .

	Theory for $\text{C}_{31}\text{H}_{24}\text{N}_2\text{SO}_3$		Found.	
			I.	II.
C_{31}	372	73.81	74.10	—
H_{24}	24	4.76	5.03	—
N_2	28	5.55	—	—
S	32	6.35	—	6.53
O_3	48	9.53	—	—
	504	100.00		

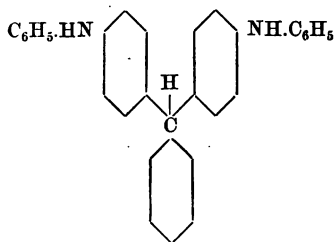
The constitution of this sulphonic acid, on the assumption that the phenyl of one of the phenyl-amido groups is attacked, may be either



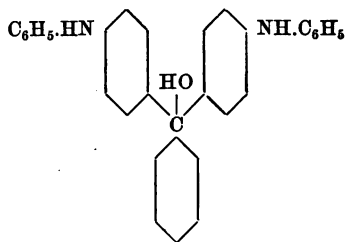
If, instead of stopping the heating with sulphuric acid at the stage indicated, the operation is prolonged till a drop of the solution gives no precipitate when thrown into water, a higher sulphonic acid, freely soluble in water with a dull bluish-green colour, is obtained. This acid is probably a disulphonic acid, but I have not as yet been able to isolate any of its salts in a state of sufficient purity to prove this by analysis. This soluble acid dyes silk of a dull-green colour, and its absorption-spectrum appears to be identical with that of the hydrochloride previously figured.

Other secondary monamines, such as $\beta\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, and $\alpha\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, when heated with benzotrichloride in presence of zinc chloride, also give green colouring matters capable of forming sulphonic acids, and the greens produced by the action of benzotrichloride upon methyl-diphenylamine and ethyl-diphenylamine likewise form sulphonic acids, whose soluble salts dye silk and wool from an alkaline bath in the same manner as the "Nicholson blues." All these "alkaline greens," although lacking in brilliancy, are extremely fast dyes, and offer considerable advantages from an industrial point of view, owing to the facility with which they can be used in admixture with the alkaline blues.

Theoretical Considerations.—Although I have at present no direct experimental evidence bearing upon the constitution of diphenylamine-green, there can, I think, be but little doubt on general grounds that it is a member of the para series, and analogy with triamido-triphenyl-carbinol or pararosanine (E. and O. Fischer, *Ber.*, 13, 2204) to which it is related, suggests the following constitutional formulæ:—

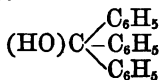


Diphenyldiamidotriphenyl-methane.
(Leuco-base of diphenylamine-green.)

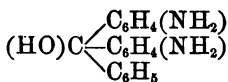


Diphenyldiamidotriphenyl-carbinol.
(Free base of diphenylamine-green.)

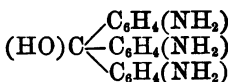
The relations of diphenylamine-green to the other colours of the rosaniline group will be obvious to those who have followed the investigations in this direction during the last three or four years. But the extreme technical importance of these bodies renders it desirable once more to point out this connection, the more especially as the new colouring matter supplies a link between pararosanine on the one hand, and triphenyl-rosaniline on the other. Thus we have the following developmental series:—



Triphenyl-carbinol.

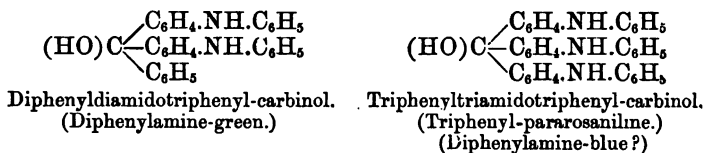


Diamidotriphenyl-carbinol.*

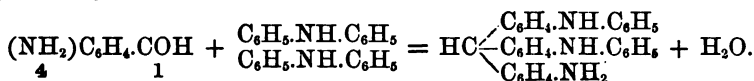


Triamidotriphenyl-carbinol.
(Pararosanine.)

* O. Doebner (*Ber.*, 15, 234).



I may here point out that two distinct kinds of "aniline blue" are found in commerce, the well-known triphenyl-rosaniline formed by the phenylation of rosaniline, and another blue of a much finer shade, and differing in certain other characters, formed by the oxidation of diphenylamine with C_2Cl_6 , or oxalic acid. From its mode of formation, this last colouring matter is most probably triphenylpararosanine, and the transition from diphenylamine-green to diphenylamine-blue could obviously be effected by forming a condensation-product with para-amidobenzaldehyde and diphenylamine, according to Fischer's method* :—



The leuco-base thus formed would on oxidation furnish diphenyl-rosaniline, and this by phenylation would pass into triphenylrosaniline. We may thus venture to hope that the aniline blues, which are industrially the most important of all the rosaniline group of colours, may at no distant period be produced by a more direct method than the phenylation of magenta.

Derivatives of Diphenyl-methane.

In purifying the crude product obtained by the action of commercial benzyl chloride upon diphenylamine in the technical operation previously described, it was found that, together with the triphenyl-methane derivatives yielding the colouring matter, there was produced a considerable quantity of some other substance which gave no colour on oxidation, and which was freely dissolved out by the toluene used for purifying the crude hydrochloride of the green base. This substance was isolated as a white amorphous powder, melting at about 89°C ., but differing totally in its appearance and properties from benzyl-diphenylamine. It appeared probable that this body was a product of the action of $\text{C}_6\text{H}_5.\text{CH}_2\text{Cl}$ upon diphenylamine at the high temperature employed, and this belief was fully justified by some further experiments, in which this reaction was performed with pure $\text{C}_6\text{H}_7\text{Cl}$ at a lower temperature in the presence of zinc chloride, and

* Compare O. Fischer's German patents, No. 16,707, Feb. 1st, 1881, and No. 16,710, Feb. 24th, 1881.

which furnished a product identical with the substance mentioned. In order to complete this part of my investigations, I therefore made a series of experiments upon the action of C_6H_5Cl upon various amines under the conditions mentioned; and although the products thus obtained were extremely unsatisfactory from a chemical point of view, I think it desirable to record the results, as these are not devoid of a certain amount of scientific interest, and I hope to be able to investigate these bodies more completely at some future time.

Action of Benzyl Chloride upon Diphenylamine.—The two substances were mixed in the proportions of one molecule each, and warmed in an open dish on a water-bath with a quantity of anhydrous powdered zinc chloride, equal to the weight of diphenylamine taken. In about an hour the mixture becomes thick and pasty, and HCl is freely given off. The reaction is stopped at this stage, the product boiled with water to remove zinc chloride, and then washed several times with warm alcohol to get rid of unaltered diphenylamine and benzyl chloride. The substance was purified by dissolving it in warm aniline and pouring the solution in a thin stream into a large quantity of alcohol, by which means it is obtained in a flocculent state. The precipitate is collected and washed with alcohol till free from aniline, and then with a mixture of aqueous hydrochloric acid and alcohol to remove the trace of green, which, as already stated, is invariably produced, even with the most carefully rectified benzyl chloride. Specimens were prepared for analysis by dissolving in cold ether, and filtering the ethereal solution into alcohol. The flocculent precipitate was collected, washed with alcohol, and dried. The following results were obtained:—

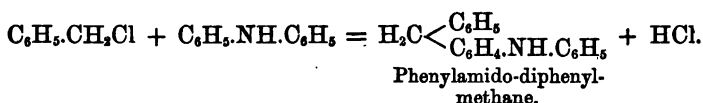
- I. 0.2100 gram burnt with CuO gave 0.6802 gram CO_2 and 0.1273 gram H_2O .
- II. 0.2419 gram burnt with CuO gave 0.7777 gram CO_2 and 0.1421 gram H_2O .
- III. 0.1220 gram burnt with CuO gave 0.3927 gram CO_2 and 0.0725 gram H_2O .

These results agree sufficiently with a formula indicating a substance isomeric with benzyl-diphenylamine.

	Theory for C ₁₉ H ₁₇ N.		Found.		
			I.	II.	III.
C ₁₉	228	88.03	88.34	87.68	87.78
H ₁₇	17	6.56	6.73	6.52	6.60
N	14	5.41	—*	—	—
	<hr/>	<hr/>			
	259	100.00			

* Several attempts were made to determine the nitrogen, both by Dumas' and by

As the substance is similar in composition to benzyl-diphenylamine, but quite different in its properties, it thus appears that when benzyl chloride acts upon diphenylamine in the presence of zinc chloride, the hydrogen of the aromatic nucleus is attacked instead of the hydrogen of the amido-group, as occurs when diphenylamine and benzyl chloride are gently warmed for some time in presence of a caustic alkali.* The present reaction, therefore, gives rise to the formation of a derivative of diphenyl-methane:—



Phenylamido-diphenyl-methane is a white pulverulent substance, readily soluble in benzene, chloroform, ether, and carbon disulphide, and insoluble in glacial acetic acid, alcohol, and acetone. It shows no tendency to crystallise from any of its solutions. The melting point of the substance is about 89° , but it softens long before this temperature. When heated with sulphuric acid, it dissolves with formation of a sulphonic acid, but no crystallisable salt could be obtained. Attempts to prepare an acetyl-derivative were unsuccessful.

When diphenylamine is dissolved in double the quantity of benzyl chloride required for the foregoing reaction, and heated to a temperature of 110° in presence of an equal weight of zinc chloride as long as hydrogen chloride is given off, a substance very similar to the last is obtained, but the analytical results showed that a second hydrogen-atom had been replaced by benzyl. The method of purification employed was the same as before.

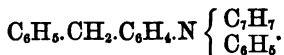
- I. 0.2131 gram burnt with CuO gave 0.6989 gram CO_2 and 0.1269 gram H_2O .
 II. 0.2321 gram burnt with CuO gave 0.7610 gram CO_2 and 0.1393 gram H_2O .

	Theory for $\text{C}_{26}\text{H}_{22}\text{N}$.		Found.	
			I.	II.
C_{26}	312	89.39	89.44	89.42
H_{22}	23	6.59	6.61	6.66
N	14	4.02	—	—
	<hr/> 349	<hr/> 100.00		

the ammonia process, but the results were somewhat too low, probably owing to the small amount of this element present and the extremely incombustible nature of the substance. The C and H determinations had all to be made by combustion in oxygen.

* See my preliminary note, already referred to (*Ber.*, 14, 1885).

This substance is, therefore, most probably benzyl-phenylamido-diphenyl-methane :—



It resembles the preceding body in its behaviour towards solvents. No definite melting point could be determined.

A body of very similar properties to the foregoing was obtained by heating benzyl chloride with methyl-diphenylamine and zinc chloride. The temperature had to be raised to about 120° before the reaction commenced. After some hours' cohobation, the evolution of HCl had ceased, and the product, after purification in the usual manner, gave a substance which was doubtless methyl-phenylamido-diphenyl-methane, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{cases} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{cases}$; but as it appeared to possess the same appearance and chemical inertness as the preceding, it was not further examined.

Action of Benzyl Chloride upon Aniline.—The investigations of Böttinger (*Ber.*, 11, 276, 840, and 12, 975; see also O. Fischer, *ibid.*, 12, 1693, and 13, 665) having shown that condensation can take place between benzal chloride and aniline, I thought it desirable to try the action of benzyl chloride upon aniline in the hope of obtaining an amido-derivative of diphenyl-methane, a substance that would probably have possessed more definite chemical properties than the preceding ones. The operation was carried out in the same manner as before, pure dry aniline hydrochloride being substituted for diphenylamine, but the mixture had to be heated to a higher temperature before any reaction set in. The contents of the flask were kept gently boiling for some hours at about 120° , and the product, after purification, gave numbers which showed that substitution had taken place both in the benzene nucleus and in the amido-group:—

I. 0.2086 gram gave 0.6815 gram CO_2 and 0.1275 gram H_2O .

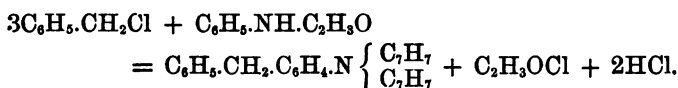
II. 0.3150 ,, 1.0339 ,, 0.1834 ,,

These results, which were furnished by the combustion of two different preparations, agree with the formula of dibenzylamido-diphenyl-methane :—

	Theory for $\text{C}_{27}\text{H}_{23}\text{N}$.		Found.	
			I.	II.
C_{27}	324	89.25	89.10	89.51
H_{23}	25	6.89	6.79	6.47
N	14	3.86	—	—
	<hr/>	<hr/>		
	363	100.00		

$\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \left\{ \begin{smallmatrix} \text{C}_7\text{H}_7 \\ \text{C}_7\text{H}_7 \end{smallmatrix} \right.$ is a substance resembling the preceding ones in its appearance and general characters. It is somewhat less soluble in benzene and toluene, and its solutions exhibit a marked blue fluorescence.

The foregoing reaction was repeated with acetanilide. At about 120° a brisk reaction takes place, and clouds of HCl are given off. On purifying the product by the usual method, and making a combustion, it was found to be identical with the last, so that the acetyl-group had been replaced by benzyl:—



0.2292 gram gave 0.7484 gram CO_2 and 0.1389 gram H_2O .

	Theory.	Found.
C	89.25	89.05
H	6.89	6.73

The diphenylmethane-derivatives described in the present paper are all whitish uncrystallisable powders, which, although devoid of any striking chemical characteristics, are doubtless perfectly definite bodies. These investigations thus show that when benzyl chloride acts upon amines at a high temperature, or at a lower temperature in presence of zinc chloride, the hydrogen of the aromatic nucleus is attacked; and in cases where the amido-group contains any replaceable hydrogen or other radicle, substitution likewise takes place in this group, with formation of substituted amido-derivatives of diphenylmethane. The liquid base described by Michler and Gradmann (*Ber.*, 10, 2078), as resulting from the action of benzyl chloride upon dimethylaniline at a high temperature, no doubt belongs to this series, and is most probably dimethylamido-diphenyl-methane, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2$. Some of this base was prepared, but it could not be purified sufficiently for analysis.

XXXII.—*Contributions to the Chemistry of Cerium Compounds.*

By W. N. HARTLEY, F.R.S.E., &c., Professor of Chemistry, Royal College of Science, Dublin.

(1.) *On the Preparation of Pure Cerium Salts.*

IN studying the compounds of cerium, my original purpose was to establish the value of the atomic weight of the element, and to ascertain definitely the number of salt-forming oxides which it could yield. Much of the earlier work was accomplished prior to the year 1877; but while the investigation was in progress, Bührig in 1875 (*J. pr. Chem.*, 12, 230) determined most accurately the combining weight, and Messrs. Hillebrand and Norton in 1876 (*Pogg. Ann.*, 156) prepared the metal. Its specific heat was determined by Hillebrand (*Pogg. Ann.*, 163, 71—87), so that further work in this direction was rendered unnecessary. For several reasons the phosphates of cerium appeared to be worthy of attention, and as the following communications regarding certain of these compounds have been in my hands for some years, I have no desire to reserve them for a more complete study.

Pure cerium salts were obtained by two methods, that of Mosander and that of Bunsen and Bahr. Mosander's process consists in saturating with chlorine a precipitate of cerous hydroxide suspended in strong potash solution, allowing the precipitate some days to digest, with frequent shaking, finally syphoning off the clear solution, washing the precipitate with water, dissolving in hydrochloric acid, and repeating the process about three times. Bunsen and Bahr's process depends upon the precipitation of a basic ceric sulphate, when a ceric nitrate in solution is poured into a large volume of dilute sulphuric acid. This operation was performed several times on the same material. The following is evidence of the purity of the salts used. A concentrated solution of cerous chloride in a test-tube, 1 inch in diameter, showed no trace of either a didymium or erbium absorption-band. According to the determination of Bührig, detailed in the paper already quoted, there must have been less than $\frac{1}{18000}$ th of didymium present in the liquid. The absence of lanthanum was proved by the largest and strongest lines of that element being absent from the spark-spectrum of the solution when the visible rays were examined. The cerium lines were of course seen.

Not content, however, with this test, I have submitted the specimen of ceric phosphate mentioned further on, to a more searching spectroscopic analysis. The salt was dissolved in strong hydrochloric acid, and

the solution which contained 10 per cent. of cerium was submitted to the action of a condensed spark. The spectrum which extends from a line with a wave-length of 4500 to the extreme ray No. 25 of cadmium (wave-length 2217.6) was photographed on a gelatine plate in the instrument, and by the method described by me (*Sci. Pro. Soc. Dublin Society*, 3, 1881). The lines observed were over 450 in number, about 66 of which belonged to the air-spectrum. Solutions of didymium and lanthanum, containing 10 per cent. of the metals in the former case, and about this in the latter, were photographed in the same plate. The strongest and longest lines were not observed in the cerium spectrum, but an unexpected result was obtained. A trace of beryllium was shown by an indication of the strong line 3130—3130.4 (Cornu's map, *Annales de l'École Normale*, 1881). The quantity was estimated to be less than $\frac{1}{100}$ th of a per cent.

Although the visible spectrum showed no trace of yttria in this salt, nevertheless a few lines short and faint, belonging to this element, were remarked in its photograph. This is evidently a tolerably pure preparation.

(2.) A Delicate Test for Cerium.

Since we may readily detect didymium in cerium salts by means of the spectroscope, I thought that it would be advantageous to have a method as simple and efficacious for detecting cerium in the presence of lanthanum and didymium, avoiding the addition of non-volatile salts to the solution. An elegant reaction, which fulfils this desirable end, is made in the following manner: To the solution to be examined, which may be either slightly acid or neutral, is added a solution of ammoniac acetate and a little hydrogen peroxide. When much cerium is present a brownish-red coloration results, which in a few minutes darkens considerably; a brisk shaking then causes the liquid to gelatinise, from the formation of a ceric acetate, probably the basic salt analysed by Erk (*Zeitschr. f. Chem.* [2], 8, 100). The lanthanum and didymium remain for the most part in solution, and may be evaporated by the addition of water and filtration. Should the proportion of cerium be small, the liquid will remain yellow without the cerium being precipitated, and it sometimes happens that the filtrate from a copious precipitate remains yellow. In such case gently warming the liquid to about 40° or 60° will cause the dissolved acetate to separate without undergoing reduction and consequent resolution. The delicacy of the reaction of cerium salts with an alkaline acetate and hydrogen peroxide, was tested in the following manner: A solution of 0.25 gram of ceric potassic nitrate was dissolved in 100 c.c. of water, and reduced to the condition of a cerous salt by sulphurous acid. The

nitrate has the composition $\text{CeN}_4\text{O}_{12}, 2\text{KNO}_3, 4\text{H}_2\text{O}$ (at. wt. of Ce = 141.2), and this solution contained one part of cerium in 2000 of water. When 2 c.c. of the liquid were diluted with water to 100 c.c. the addition of ammonium acetate and hydrogen peroxide yielded a precipitate which was easily filtered, washed, dried, ignited, and weighed. It yielded an amount of ceric oxide equivalent to 0.001 gram of cerium. Hence we can separate one part of cerium from 100,000 parts of liquid.

Attempts were made to apply this method to the quantitative estimation of cerium and its separation from lanthanum and didymium. The results were not satisfactory; thus, from three portions of a solution of cerite, each containing 0.2268 gram in 100 c.c., three precipitates were obtained, weighing 0.08—0.081 and 0.082 gram, corresponding to 33.65—34.03 and 34.44 per cent. of Ce_2O_3 . It was proved that the basic ceric salt is not precipitated free from didymium when this substance is largely present; also that a precipitate of a white, or rather a greyish colour, was formed by the addition to a pure didymium salt of an alkaline acetate containing free acetic acid, and subsequently hydrogen peroxide. The yellow colour yielded by this reaction is of itself a valuable test for cerium.

(3.) *The Preparation and Analysis of Cerous Phosphates.*

Where pure cerous chloride or nitrate is precipitated by phosphate of soda, a precipitate of cerous phosphate is formed, which varies in physical properties to some extent with the conditions under which the operation is performed. Although there appears to be no variation in the composition of the precipitate, yet the practicability of obtaining a pure and dry substance from it is greatly affected. Sometimes the precipitate is slimy, and as it remains suspended in the liquid it is impossible to wash it by decantation, while it is at the same time equally impossible to filter it from the liquid, since it renders filter-paper waterproof. On other occasions it takes the form of a light and finely divided powder, which passes with great readiness through any filter. In order to work to the best advantage, acidify the sodium phosphate solution with hydrochloric acid, and add a small quantity of sulphurous acid to the cerous chloride solution, in order to obtain all accidentally oxidised salt in the reduced state. After precipitation gently warm, but do not boil the liquid. The insoluble phosphate readily settles down, and may be repeatedly washed by decantation until the washings are free from any acid reaction, free from chlorine, and on evaporation incapable of leaving a solid residue.

Several preparations were made in this way; the precipitates partially dried on the filter were detached and placed over oil of vitriol

contained in an air-pump bell-jar. It is characteristic of this substance that it dries up to a hard porcelainous mass, of a somewhat conchoidal fracture and glazed surface. Its colour is white. The specimens were powdered up and analysed.

The estimation of water was made with separate portions because ignition is necessary, and the ignited phosphate is practically insoluble even in strong acids. The substance is hard and powdered with difficulty. It dissolves readily in strong hydrochloric and nitric acids, yielding solutions of a cerous salt. It is not converted into a ceric compound by ignition.

It is not considered necessary to enter into a detailed description of the method of analysis employed, since Jolin (*Bull. Soc. Chim.* [2], 21, 540) has described a compound obtained by adding orthophosphoric acid to a solution of cerous chloride, which has the same composition, though it differs in physical properties. Jolin's phosphate was in fact an amorphous precipitate.

Composition of Cerous Phosphate.

	I.	II.
Ce ₂ O ₃	58.30	58.60 per cent.
P ₂ O ₅	26.38	26.33 „
H ₂ O	14.46	14.44 „
	<hr/>	<hr/>
	99.14	99.37 „

The formula which I assign to the salt is—



requiring:—

	Mol. weight.	Per cent.
Ce ₂ O ₃	330.52	60.69
P ₂ O ₅	142.00	26.08
H ₂ O	72.00	13.23
	<hr/>	<hr/>
	544.52	100.00

The deficiency in cerous oxide found by the above analysis was probably caused by precipitation of the cerous oxalate, from a hot solution of the salt in hydrochloric acid.

(4.) *The Preparation and Analysis of Ceric Phosphate.*

In precipitating solutions of ceric nitrate or sulphate with sodium phosphate, in order to prepare ceric phosphate, the reaction was made under different conditions.

In one case the sodium phosphate, gently acidified with nitric acid, was added in excess of the amount necessary to throw down all the

cerium while in another, ceric nitrate was kept in excess. The same precipitate was formed in each case.

By using an excess of sodium phosphate a slimy yellow precipitate is formed, which, when dried at 60° in an open dish, is of a pale canary-yellow colour, opaque, and easily powdered. It shows an acid reaction with litmus-paper when moistened, and it liberates iodine from potassium iodide without the addition of an acid.

Preparation A.—Sodium phosphate acidified with sulphuric acid was added in excess to a solution of ceric sulphate. The precipitate was very carefully washed and dried in an open dish at 60° .

Estimation of water.—I. 0.543 gram of substance heated to redness in a platinum crucible lost 0.138 gram in weight = 25.41 per cent. of water. Four other estimations were made with the following results:—

	II.	III.	IV.	V.
Weight of substance taken	2.2840	1.1308	2.00	0.30
Loss at 100°	0.3844	0.1834	0.36	0.0501
Per cent. of water,	16.87	16.21	18.00	16.70
Loss on heating to 360°	—	0.2601	0.5055	—
Total amount of water per cent.	—	23.00	25.27	—

Mean total amount of water found by analyses I, III, and IV = 24.56 per cent.

Water lost at 100° —mean of analyses II, III, IV, and V = 16.94 per cent.

Estimation of Ceric Oxide.—The cerium was estimated in two ways. 1st. By precipitation as cerous oxalate from an acid solution, after reduction of the ceric to a cerous salt by boiling with sulphurous acid. The oxalate was weighed, then ignited and weighed again. 2nd. By means of iodine liberated from potassium iodide, when brought in contact with the phosphate and hydrochloric acid, the free iodine being estimated volumetrically by solution of sodium thiosulphate. Each atom of active oxygen was regarded as being equivalent to CeO_2 ($\text{Ce} = 191.12$).

Estimation of Cerium by Precipitation as Oxalate and subsequent Ignition.—1.53 grams of substance were dissolved in hydrochloric acid and made up to the volume of 150 c.c., by the addition of water. One-sixth of the liquid was taken for each estimation, being equivalent to 0.255 gram of substance.

	CeO_2 Amount found.	CeO_2 per cent.
I	0.1118 gram	43.84
II	0.1100 „	43.73

Mean = 43.77 per cent.

After drying at 100° .

Estimation of the Active Oxygen in the Compound, and Deduction therefrom of the amount of CeO_2 .

	Weight of substance taken.	Active oxygen found.	CeO_2 found.	CeO_2 per cent.
I.....	1.0420	0.02092	0.4445	42.66
II.....	1.0400	0.02054	0.4461	42.90

Mean = 42.78 per cent. CeO_2 .

Estimation of the Phosphoric Acid.—Three equal volumes of a solution of the ceric phosphate in nitric acid, measuring 100 c.c., each containing 0.1 gram of the phosphate, were precipitated by ammonium molybdate, and afterwards, the phospho-molybdate precipitate being dissolved in ammonia, the phosphoric acid was precipitated therefrom by addition of magnesia mixture.

	I. gram.	II. gram.	III. gram.	IV. gram.
Substance taken ..	0.1	0.1	0.1	0.1
$\text{Mg}_2\text{P}_2\text{O}_7$ found....	0.0484	0.049	0.8484	0.0464
P_2O_5 found	0.03095	0.0315	0.03095	0.02967
P_2O_5 per cent.	30.95	31.5	30.95	29.67

Mean 31.13 per cent. P_2O_5 , if we reject the last determination, which is evidently too low.

Preparation B.—A solution of sodic phosphate, *not acidified*, was added in excess to a solution of ceric nitrate. The precipitate was dried at once at 100° , the desiccation at 60° being slow and tedious.

Estimation of Water by Ignition.

	Weight of substance taken.	Loss on ignition.	Water per cent.
I	0.7739	0.0628	9.17
II	0.1814	0.0164	9.04

Mean = 9.10 per cent. water.

Estimation of Ceric Oxide.—This was effected by determination of the active oxygen in the substance only. It was found advantageous to use ammonio-ferrous sulphate as the reducing agent, and to determine the excess of ferrous salt by potassic permanganate, freshly standardised in the usual way. The oxidation caused by the ceric salt is instantaneous and complete. 1.1406 grams of ceric phosphate were dissolved in strong sulphuric acid and diluted to 1 litre. Identical numbers were obtained when equal volumes of this solution were taken. Thus, in the two first analyses:—

	gram.	gram.
Weight of substance taken..	0·11406	0·11406
Active oxygen found	0·0028	0·0028
CeO ₂ calculated.....	0·0595	0·0595
CeO ₂ per cent.	52·16	52·16

Preparation C.—A deficiency of a solution of sodic phosphate, acidified by nitric acid, was added to a solution of ceric nitrate. The precipitate was most carefully washed and partially dried on a filter by exposure to the air. Desiccation was completed by transferring the substance to a dish and allowing it to remain some months in an exhausted bell-jar, containing a vessel holding oil of vitriol. The product was a translucent material, like dark-coloured amber in appearance. It was brittle, and powdered like ordinary rosin, giving a canary-yellow powder.

Estimation of Water.

	Weight of substance taken. gram.	Loss on ignition.	Water per cent.
I	0·5266	0·1552	29·47
II	0·1582	0·0476	30·08

Mean = 29·77 per cent. H₂O.

Estimation of Cerium.—By precipitation as cerous oxalate.

0·1854 gram yielded 0·083 gram CeO₂ = 44·76 per cent. CeO₂.

By the oxidation of ammonio-ferrous sulphate.

Three determinations made with separate quantities of a solution, each containing 0·0927 gram of the cerium salt, yielded the same result, viz. :—

Active oxygen.	CeO ₂ .	CeO ₂ per cent.
0·001847	0·03925	42·34

Mean result of both methods 43·55 per cent. of CeO₂.

Estimation of Phosphoric Acid.—6·705 grams were dissolved and made up to a volume of 250 c.c. Two portions, each containing 50 c.c. of the liquid = 0·141 gram of substance, were taken, and they yielded :—

	Mg ₂ P ₂ O ₇ .	P ₂ O ₅ .	P ₂ O ₅ per cent.
I	0·0620	0·0393	28·87
II	0·0595	0·0377	26·75
III	0·0597	0·0378	26·80

Mean proportion of P₂O₅ = 27·14 per cent.

This latter preparation, which was dried without the aid of heat, contains about 5 per cent. more water than preparation A, but the

ratio of phosphoric acid to cerium in it is evidently the same, notwithstanding that the strict proportion shows some difference.

The proportions of P_2O_5 to CeO_2 stand thus in the three preparations :—

A. $P_2O_5 : CeO_2 :: 1 : 1.36$

B. $P_2O_5 : CeO_2 :: 1 : 1.34$

C. $P_2O_5 : CeO_2 :: 1 : 1.60$

Preparation C was in all respects the most definite substance, and it is therefore best to calculate a formula from its composition.

From the mean numbers expressing the composition of preparation C may be deduced the formula $(CeO_2)_4(P_2O_5)_3.26H_2O$.

Composition of Hydrated Ceric Phosphate.

	Mol. weight.	Calculated per cent.	Found per cent.
H_2O	468.0	29.50	29.77
CeO_2	692.8	43.66	43.55
P_2O_5	426.0	26.84	27.14
	<hr/> 1586.8	<hr/> 99.99	<hr/> 100.46

The Composition of Ignited Ceric Phosphate.

	Found.	Calculated for $(CeO_2)_4(P_2O_5)_3$.
CeO_2	61.607	61.5 per cent.
P_2O_5	38.393	38.5 „
	<hr/> 100.000	<hr/> 100.0

I conclude from the foregoing experiments that there is only one ceric ortho-phosphate, and that in the anhydrous state it has the composition expressed by the formula $(CeO_2)_4(P_2O_5)_3$, and when dried in a vacuum it is $(CeO_2)_4(P_2O_5)_3.26H_2O$, or what is more probable—



XXXIII.—*The Analysis of Rhabdophane, a New British Mineral.*

By W. N. HARTLEY, F.R.S.E., &c., Professor of Chemistry, Royal College of Science, Dublin.

THIS mineral, which was discovered by my friend, Mr. W. G. Lettsom, has a somewhat remarkable history. The exact locality of its matrix is unknown. It occurs in small irregular mammelated concretions of a dull garnet-red colour, and it is translucent. For more than sixty years two specimens of this substance existed in the collection of the late Mr. Turner (subsequently the property of the late Mr. Ludlam), and are described in the catalogue published in 1837 by Mr. Heuland as *Zinc Sulfuré, mameloné de Cornouailles*. Among the blendes in the collection at Oxford, Professor N. S. Maskelyne has found recently two more specimens labelled "from Cornwall." This mineral contains neither zinc nor sulphur.

When engaged in examining various specimens of British blendes for the information of M. Lecocq de Boisbaudran in his search for sources of the metal gallium, Mr. Lettsom recognised the bands of didymium by examining with a pocket spectroscope the light reflected from the substance. The characteristic spectrum is easily seen when any didymium compound is so examined, even if the mineral be of a yellow or dark-brown colour. Some fragments of rhabdophane, weighing a little over 3 grams, were handed to me for analysis. Portions were powdered as they were from time to time required.

Analysis No. 1. Preliminary.—The mineral was dried at 100° and weighed, the operation being repeated until the weight was constant. The loss indicates the proportion of hygroscopic water. It was then heated in an air-bath to over 200° and repeatedly weighed, but as no constant weight was arrived at after 14 repetitions of the operation, ignition was resorted to. Loss on ignition represents the amount of combined water. Subsequent treatment with hot and cold water yielded no soluble matter. After solution in strong hydrochloric acid and evaporation to dryness, the mineral was twice moistened with hydrochloric acid and evaporated to dryness, treated again with hydrochloric acid and water, and the liquid filtered; the residue was silica. During these evaporations the acid vapours evolved were repeatedly tested for the presence of hydrofluoric acid, a dial glass being suspended over the platinum dish in which the evaporation took place, and though this was moistened with water, no silica was deposited. The solid residue, after evaporation, took a greenish-yellow tint, which disappeared on the addition of water. There was no

precipitate with sulphuretted hydrogen. The cerium metals were precipitated from their hydrochloric acid solution by means of an excess of ammonium oxalate, after the manner of Dr. Wolcott Gibbs. The oxalates, of which there was an abundant precipitate, might contain cerium, lanthanum, didymium, yttrium, erbium, terbium, thorium, and possibly zirconium.

Zirconium oxalate is soluble in solutions containing free oxalic acid, and in ammonium oxalate. The filtrate evaporated down was mixed with ammonium acetate and boiled. Scarcely a trace of ferric or aluminic phosphate was precipitated. Zirconium, thorium, and beryllium were absent, or, in other words, they would be contained in this small precipitate. The liquid was mixed with ammonia till decidedly alkaline, and allowed to stand for 24 hours; a very slight precipitate formed, which might be magnesium and beryllium phosphate. The filtrate, containing all the phosphoric acid, possibly with alkalis, was mixed with magnesia mixture. The ammonio-magnesium phosphate is apt to contain basic magnesium oxalate, when precipitated from solutions containing much oxalic acid; this, as is well known, leads to inaccuracies. The precipitate therefrom, after filtration, was redissolved in hydrochloric acid, and again precipitated by addition of ammonium chloride and ammonia, the liquid being allowed to stand for 36 hours. The precipitate, after ignition, was weighed as magnesium pyrophosphate, making the necessary correction for the amount of phosphoric acid in the filtrate and washings. The precipitate containing the cerium metals was weighed, ignited, and dissolved in sulphuric acid. The ceric salt was reduced to a state of a cerous compound by addition of sodium sulphite, and boiling off the excess of sulphurous acid. After careful neutralisation, the cerium, lanthanum, and didymium were precipitated by a saturated hot solution of sodic sulphate. The solution was allowed to stand for 24 hours, some powdered sodium sulphate being added. The crystals were then filtered off and washed with a cold saturated solution of sodic sulphate. The filtrate might contain yttrium, erbium, and terbium. After acidifying with hydrochloric acid and boiling, ammonium oxalate was added in excess to the solution; a slight precipitate formed, which was filtered off, dried on the filter, and ignited and weighed. The salt, on ignition, turned pale yellow, and remained so after cooling. In order to ascertain whether this yellow oxide contained erbium, it was dissolved in hydrochloric acid. Taking as concentrated a solution as possible, a layer of liquid of 2 cm. in thickness was examined with the spectro-scope, but the remarkable absorption-band in the green part of the spectrum, characteristic of erbium, was absent. The salt was then evaporated to dryness and tested on a platinum wire in a Bunsen flame, but no spectrum of erbium was observed. It was not a

didymium compound which had escaped precipitation by the sodium sulphate, since in that case the oxide would have been brown, and the solution would have exhibited the remarkable absorption-spectrum. It yielded no reaction with ammoniac acetate and hydrogen peroxide; therefore, cerium was not present in the solution. In the absence of cerium and didymium, the presence of lanthanum is not probable. There was too small a quantity of substance to make any number of reactions to prove the presence of yttrium; the spark-spectrum was therefore examined, and the presence of yttrium only was proved. No alkalis were detected with the spectroscope, and the alkaline earths were proved to be absent from the mineral. The metals cerium, didymium, and lanthanum, were detected in the precipitate, separated by sodium sulphate. The crystalline double sulphates were dissolved in hydrochloric acid, and after addition of caustic potash, the liquid was saturated with chlorine; after standing, the clear liquid was syphoned off, and the operation was repeated again and again, until the liquid showed only a faint trace of the didymium bands. The undissolved residue was ceric hydrate; it was readily soluble in hydrochloric acid with evolution of chlorine, the result being a solution of cerous chloride. This was reprecipitated in the form of oxalate, and weighed as such, ignited, and again weighed as ceric oxide.

To determine the non-metallic constituents, some portions of the mineral free from gangue were dissolved in nitric acid; there were no halogens present nor sulphuric acid, but a copious precipitate was obtained with ammonium molybdate. There was not the slightest effervescence upon treatment with acid.

Four subsequent examinations of different portions of the specimen have yielded similar results, the differences being in the occurrence of small quantities of iron, alumina, lime, and magnesia derived from the gangue, and slight variations in the proportions of silica.

In the case of this analysis, the following numbers were obtained:—

Weight of substance taken for analysis = 0.6378 gram.

	gram.	Per cent.
Loss on ignition = total water	0.0572	9.34
Silica	0.0023	0.36
Al ₂ O ₃ , Fe ₂ O ₃ with P ₂ O ₅	0.0014	0.21
Magnesium phosphate	0.0071	1.09
Cerous oxide	0.1479	23.19
Lanthanum and didymium oxides	0.2217	34.77
Yttrium oxide	0.0133	2.09
Phosphoric anhydride	0.1578	24.77
		<hr/> 95.82

In the analysis of this mineral, it was necessary to add a large excess of ammonium oxalate, and allow the liquid to stand at least 24 hours, in order to separate every trace of the cerium metals. As the excess of the ammonium oxalate is not very soluble, it readily separates out during the concentration of the solution, previous to the precipitation of the phosphoric acid. The clear solution should be poured off from the separated crystals of oxalate, the crystals should be washed with cold water, and the washings added to the original liquid. The ammonium oxalate thus separated is then ignited with sodic carbonate to yield up every trace of phosphoric acid it may contain, so that it may be returned in the state of ortho-phosphate.

In two determinations the phosphoric acid was precipitated from the dilute solution remaining after filtration from the oxalates of the cerium metals, the precautions recommended by Fresenius being observed; and after filtration, a correction was made for the solubility of the magnesium ammonium phosphate in ammonia and ammonium chloride solution.

Two analyses were made with small quantities of the mineral, chiefly with the view of ascertaining the proportion of the cerium metals and phosphoric acids present. The latter constituent was estimated by precipitation with uranic acetate, a method which did not prove altogether satisfactory, since a small portion of the phosphate separated out from the filtered liquid after it had been standing for some days. This portion was collected separately, and its weight was added to that of the larger portion.

Analysis of Mineral.

	II. gram.	III. gram.
Weight of mineral taken.....	0.3394	0.3724
Loss on drying at 100°	0.0045	0.0046
Moisture = 1.32 per cent.		
Weight of dried mineral.....	0.3349	0.3678
Weight after ignition	0.3049	0.3348
Loss (combined water)	0.0300	0.0330
Silica	0.0059	0.0030
Cerium, lanthanum, and didymium oxalates	0.4277	0.4669
Uranic phosphate	0.3890	0.4255
Phosphoric anhydride	—	—

Composition of Mineral when dried at 100°.

	II. Per cent.	III. Per cent.
Water	8.96	8.94
Silica	1.76	0.815
Ce ₂ O ₃ , La ₂ O ₃ , Di ₂ O ₃	59.00	58.24
P ₂ O ₅	25.67	24.87
	<hr/> 95.39	<hr/> 92.865

A fourth analysis was executed with a larger quantity of the mineral. After separation of the oxalates, the liquid was evaporated down and heated with sodium carbonate to destroy the oxalic acid, eliminate the ammonia, and retain the phosphoric acid in the condition of ortho-phosphate. The saline mass was redissolved, acidified with hydrochloric acid, made alkaline with ammonia, and treated with magnesia mixture; the numbers yielded were the following:—

	gram.
Weight of mineral	0.9166
The same after being dried at 100°	0.8996
Loss (moisture)	0.0170
Weight of mineral dried at 100°	0.8996
The same after ignition	0.8323
Loss (combined water)	0.0673
Silica	0.0338
Al ₂ O ₃ , Fe ₂ O ₃ , CaO, MgO with P ₂ O ₅	0.0174
P ₂ O ₅ (from 0.3466 gram Mg ₃ P ₂ O ₈)	0.2217
Ce ₂ O ₃ , La ₂ O ₃ , Di ₂ O ₃ , and Yt ₂ O ₃ (from 1.1388 gram of oxalates)	0.5550

Composition of Mineral.

	Per cent.
Combined water	7.50
Silica	3.76
Al ₂ O ₃ , Fe ₂ O ₃ , CeO, MgO, with P ₂ O ₅	1.93
P ₂ O ₅	24.64
Ce ₂ O ₃ , La ₂ O ₃ , Di ₂ O ₃ , and Yt ₂ O ₃	61.69
	<hr/> 99.52

Constitution of Rhabdophane.

With regard to the constitution of the mineral it is evidently of the same character as the artificial cerous phosphate I have described. It, however, contains at least four bases with nearly the same salt-form-

ing properties, but with slightly different atomic weight, viz., Ce = 141.2, La = 139, Di = 147.8, Yt = 92.5.

Now, 93.83 per cent. of the mineral consists of the hydrated phosphates of these bases. If, therefore, we eliminate the impurities and recalculate the composition of the phosphates, at the same time comparing the figures with those derivable from a calculation of similar phosphates of the cerium metals, we arrive at the following result:—

Weight of dried mineral = 0.8440.

	Found.	Per cent.
Combined water	0.0673	7.97
P ₂ O ₅	0.2217	26.26
Ce ₂ O ₃ , &c.	0.5550	65.75
		<hr/> 99.98

Calculated.

Ce ₂ O ₃ , P ₂ O ₅ , 2H ₂ O.			Di ₂ O ₃ , P ₂ O ₅ , 2H ₂ O.			La ₂ O ₃ , P ₂ O ₅ , 2H ₂ O.		
	Mol. weight.	Per cent.		Mol. weight.	Per cent.		Mol. weight.	Per cent.
H ₂ O ..	36.0	7.08	H ₂ O ..	36	6.92	H ₂ O ..	36	7.14
P ₂ O ₅ ..	142.0	27.95	P ₂ O ₅ ..	142	27.30	P ₂ O ₅ ..	142	28.17
Ce ₂ O ₃ ..	330.4	64.96	Di ₂ O ₃ ..	342	65.77	La ₂ O ₃ ..	326	64.68
		<hr/> 99.99			<hr/> 99.99			<hr/> 99.99

From the relation of the calculated numbers to those found by analysis, and the fact that I have obtained a cerous phosphate, Ce₂O₃, P₂O₅, 4H₂O, which retains these 4 mols. of water after being heated to 100°, the greater part of which requires a red heat for its removal, I conclude that there are fair grounds for assigning to rhabdophane a composition such as may be described by the following formula: R₂O₃, P₂O₅, 2H₂O, in which the four metals, Ce, Di, La, or Yt, may wholly or in part replace each other.

(6.) *On the Spectrum of an Yttrium Salt obtained from Rhabdophane.*

The spectroscope consisted of one of Mr. Rutherford's fine diffraction gratings containing 17,460 lines within the inch. It was mounted on a stand with a fixed position for both collimator and telescope, the grating being movable by an arm which records angular measurements on a divided arc. The errors which could be introduced into measurements by want of perfect rigidity in the instrument, were reduced to a minimum by exercising special care in its use.

The value of the arc divisions in tenth-meters was calculated for

different parts of the scale, from measurements of lines of known wave-lengths, such as those of Li, Na², Na¹, Tl, and Sr (blue), seen in flame-spectra, and of Cd in the case of spark-spectra. The readings on the arc were certainly correct in the case of bright lines to 0.003°, and the mean error in readings made consecutively for the same line was not greater than 0.001 of a degree.

A series of measurements was made of the lines due to air, to platinum, and to the elements of hydrochloric acid, seen when condensed sparks were passed between platinum wire electrodes moistened continually with hydrochloric acid. These lines and bands were eliminated from the spectra of metallic solutions subsequently examined. Two series of spark-spectra were measured, namely, one series obtained from the bases associated with cerium which were precipitated by sodic sulphate, and another from the base supposed by its reactions to be yttria.

The precipitate yielded by sodium sulphate was dissolved in hydrochloric acid and precipitated by ammonium oxalate; the oxalates were ignited, dissolved in hydrochloric acid, and evaporated to dryness, and water was added to produce a concentrated solution. This solution was examined and the absorption-spectrum of didymium was readily seen, but there was no trace of the erbium band. On strongly igniting a portion of the salt in a gas blowpipe on platinum wire, no emission spectrum of erbium was recognised. It was not expected, however, that erbium would be found in this portion of the bases. The liquid was placed in one of Delachanel and Mermet's tubes, and a condensed spark was passed between platinum electrodes. The coil employed yields a 6-inch spark in air, and the Leyden jar has a total conducting surface of 144 square inches. The lines of lanthanum were easily recognised, the pair in the green, 5187—5182, were measured, and likewise the group in the blue, 4663—4620—4579—4557. Special reference was made to Thalén's measurements of the lines of scandium (*Compt. rend.*, 91, 45), but there was nothing corresponding to any of them to be seen. The cerium and didymium lines of course were visible, but there was a total absence of the strongest and longest lines of thorium and zirconium.

The base supposed to be yttria was twice submitted to the action of sodium sulphate after the first separation of the cerium bases, for it was found that one precipitation of the cerium was not sufficient for the complete purification of the yttrium salt. After converting the yttria into yttrium chloride, a minimum of water was used for its solution. A condensed spark showed a superb spectrum, consisting of three principal groups of lines, one of sunset-red, one of orange, and one of green, characteristic of yttrium.

Accurate measurements of the lines were made and compared with

the last series of wave-lengths of lines ascribed by Thalén to yttrium. (Om spektra tillhörande Yttrium, Erbium, Didym, och Lanthan. *Kongl. Svenska Akademiens Handlingar*, 12, 4.) There was a complete absence of any lines which could be attributed to erbium. On the other hand, all the lines capable of being accurately measured showed either a close approximation to, or a coincidence with the lines in the spectrum of yttrium, with the exception, however, of a group of closely adjacent four green lines which, under a low magnifying power or when not perfectly focussed, are not resolved, but appear as one line. I have not yet been able to connect these four lines with the spectrum of any known element.

In the following tables I give (1) a list of the lines in the spectrum of yttrium, which I observed and measured; (2) a list of lines observed by Thalén, and assigned by him to yttrium, which did not appear in the spectrum of my preparation. The wave-lengths of certain lines of feeble character, which I could not account for, were approximately 5883—5821—5805—5767—5747—5710—5634—5598—5590—5586. They were yellow, yellowish-green, and pale green; their low intensity and badly defined appearance made them difficult of measurement. The individual lines of the quadruple group in the green were capable of more accurate measurement, and appear to have the following wave-lengths:—5483—5480—5478 and 5475.

A pair of lines, 5590 and 5586, would give a mean measurement of 5588, which corresponds with a line given by Thalén in his first description of the yttrium spectrum. This has since been identified with erbium, and the more recent number is 5587.5. Some of the numbers first quoted approximate the wave-lengths of certain lines in the erbium spectrum, but as none of the strong lines of the erbium appear, they cannot be attributed to that element, but it is just possible that some substance present in minute quantity is common to Höglund's preparation of erbium, examined by Thalén, and this preparation of yttrium. I avoid as far as possible giving the wave-lengths calculated by myself for yttrium, because I regard Thalén's as the standard numbers.

(1.) *Yttrium Lines seen in the Spectrum of Yttrium Chloride prepared from Rhabdophane.*

On Thalén's scale of intensity 1 is the highest and 6 the lowest degree.

Wave-lengths (Thalén).	Intensity.	Wave-lengths. (Thalén).	Intensity.
*6613·0	3	6018·5	3
6434·5	2	6002·5	2
6313·0	6	5986·5	1
6296·0	6	5970·5	1
6273·0	6	† 5742·5	5
6236·0	5	5727·5	4
6217·5	4	5705·5	6
6199·2	4	5662·0	1
6190·5	1	5647·0	5
6181·0	3	5604·5	3
† 6163·5	2	5509·0	2
6149·0	2	5502·5	4
6131·0	1	5402·0	1
6126·0	6	5288·0	4
† 6114·0	5	5205·0	1
6106·5	5	5199·5	1
6095·0	5	5087·5	1
6088·0	5	4899·5	1
6071·0	5	4881·0	1
6053·0	5	4854·0	1
6036·0	4	4505·0	4

* Lines seen, but of which no measurements were recorded.

† A closely adjacent pair, with wave-lengths about 6163—6159·5.

‡ A similar pair, with wave-lengths about 6116—6108.

In addition to the above there were six lines in the violet, the difficulty in measurement of which was too great to give certainty to the results.

(2.) *Lines observed by Thalén and ascribed to Yttrium, which are absent from the Spectrum of the Salt obtained from Rhabdophane.*

Wave-lengths (Thalén).	Intensity.	Wave-lengths (Thalén).	Intensity.
6221·5	5	5496·0	1
6206·0	6	5479·5	3
6137·0	6	5473·0	3
6022·5	6	5468·0	6
6008·5	6	5466·0	2
5774·0	4	5437·0	4
5742·5	5	5423·5	5
5674·0	6	5416·0	6
5643·0	5	5379·0	5
5629·0	3	5320·0	5
5580·5	2	5239·5	4
5576·0	3	5195·5	4
5566·5	5	5134·5	4
5555·5	5	5122·5	2
5544·5	3	5118·0	3
5543·0	3	4981·5	4
5526·0	3	4973·0	6
5520·0	3	4859·0	5
5512·0	6	4852·0	5

There are 13 other lines which were not identified, but they are all of greater refrangibility than 4854.

The lines identified with yttrium were about 48 in number, of which 37 were satisfactorily measured; they varied in intensity from 6 to 1, and even the feeble rays in many cases were measured with accuracy.

I will quote a few consecutive wave-lengths obtained by me for comparison with those of Thalén, in evidence of the fact that the spectrum under observation was strong enough to display even the weakest lines to advantage.

Wave-lengths.		Intensity.
	Thalén.	
6053·0	6053·0	5
6035·5	6036·0	4
6018·0	6018·5	3
6001·5	6002·5	2
5986·6	5986·5	1

It is hardly possible that any important lines of yttrium between those with wave-lengths 6236 and 4505 could have escaped my observation, and yet there are in this region 38 lines belonging to the spectrum described by Thalén, the lines varying in intensity from 6 to 1. In

addition to those there are 13 other blue and violet rays which have not yet been identified.

Under the circumstances I am inclined to believe that the purer specimen of yttria is that which has yielded the simpler spectrum, but this is a point which unfortunately cannot be decided until the source from which the rhabdophane was procured has been rediscovered, and a supply of it obtained therefrom.

This is the first instance on record of yttrium being found in any British mineral.

XXXIV.—On Benzyl-phenol* and its Derivatives. (Part II.)

By EDWARD H. RENNIE, M.A. (Sydney), B.Sc. (London).

IN a previous paper it was suggested that, from the great resemblance between the reactions exhibited by paracresol and benzyl-phenol, the latter belongs to the *para*-series of compounds. Further investigation has fully confirmed this view. It will be convenient, however, before examining in detail the proofs of this statement, to describe some other derivatives which have been obtained.

Benzyl-phenol-sulphonic Acid.

This substance has not yet been obtained in the pure state. It evidently contains water of crystallisation, since it loses weight at 100°;

* Since this paper was written, a communication from Herr Liebmann has appeared (*Ber.*, 15, 150), in which he states that he had so far modified Paternò's method for preparing benzyl-phenol, as to use zinc chloride instead of zinc to act upon the mixture of benzyl-chloride and phenol, and he seems to consider this as something new. I may state that nearly all the material employed by me was prepared by the use of zinc chloride. Moreover, it is expressly stated in *Miller's Chemistry* (5th Edition, revised by Armstrong and Groves, Part III, p. 772) that not only aluminic and zinc chlorides, but also ferric chloride, exerts the same influence.

In the same paper the author concludes that because Zincke, by the action of benzyl-chloride on toluene, obtained chiefly *parabenzyl*-toluene, *therefore* the product of the action of benzyl-chloride on phenol is *parabenzyl*-phenol, but gives no further evidence in proof of the assertion. It has been recently shown (*Ber.*, 14, 2624) that the chief product of the action of methyl chloride on toluene in presence of aluminic chloride is *orthoxylylene*; but it would scarcely be safe to conclude therefrom that the chief product of the action of the same body on phenol must be *orthocresol*, especially as in other similar cases the preponderance of the *ortho*- or *para*-derivative is dependent upon the conditions of experiment.

at the same time, however, it partially decomposes, free sulphuric acid being easily recognised in the aqueous solution. If left over sulphuric acid it loses weight with extreme slowness.

Mono-nitro-benzyl-phenol.

If benzyl-phenol be dissolved in glacial acetic acid and the theoretical quantity of ordinary concentrated nitric acid (freed from nitrous vapours by passing a rapid current of air through it for several hours) be gradually added from a burette, keeping the mixture cool, and the resulting liquid be then poured into water, an oil separates which sometimes almost immediately, sometimes after standing for a time, becomes solid. It forms golden-yellow flattened prisms, which melt at 74–75°. It is volatile in steam. The results of analysis show it to be a mono-nitro-derivative.

0.2062 gram substance yielded 10.47 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.01309 gram = 6.34 per cent.

Theory for $C_6H_5.CH_2.C_6H_4(OH)NO_2$ = 6.11 per cent.

On boiling it with potassium carbonate and cooling the solution, the potassium-derivative crystallises out in long needles, which, when dried in air, are brick-red, but assume a very deep-red colour when dried at 110°. When dried in air, it seems to contain half a molecule of water of crystallisation:—

1.0732 gram (air-dried) lost at 110° 0.0389 gram = 3.62 per cent.

Theory for $C_6H_5.CH_2.C_6H_4(OK)NO_2 \cdot \frac{1}{2}H_2O$ = 3.26 per cent.

0.1475 gram anhydrous substance gave 0.0477 gram K_2SO_4 = 0.021382 gram K = 14.49 per cent.

0.1746 gram anhydrous substance gave 0.0554 gram K_2SO_4 = 0.02483 gram K = 14.22 per cent.

Theory for $C_6H_5.CH_2.C_6H_4(OK)NO_2$ = 14.60 per cent.

Amido-benzyl-phenol.

The nitro-derivative just described is easily reduced when boiled (in a flask attached to a reversed condenser) with tin and somewhat dilute hydrochloric acid. The solution on cooling deposits glistening scales of the hydrochloride; the mother-liquor deposits small hard crystals containing *tin*, probably a double salt. The hydrochloride is unstable, soon becoming very dark in colour if left exposed to the air in acid solution. An imperfectly purified specimen gave 15.74 per cent. of chlorine instead of 15.07 per cent. as required by theory.

On neutralising a solution of the hydrochloride with sodium carbonate and agitating with ether, the free base is easily obtained in glistening

scales, which are somewhat difficult to purify, as they apparently undergo change when exposed to the air in the moist state—

0.1229 gram substance yielded 7.15 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.00894 gram = 7.27 per cent.

Theory for $C_6H_5.CH_2.C_6H_3(OH)NH_2$ = 7.04 per cent.

Since the volatility of the nitro-compound above described, and the colour of its potassium-derivative, seemed to indicate (by analogy with ortho-nitro-phenols) that the NO_2 group occupies the ortho-position, an attempt was made to apply to the amido-hydrochloride the reaction described by Hübner and Ladenburg, and recently used by Hofmann (*Ber.*, 14, 570) in the determination of the constitution of orthonitro-orthocresol. On heating together the hydrochloride and sodium formate in molecular proportions, reaction took place, and an oily body of very peculiar odour distilled over, and almost immediately solidified. The quantity obtained, however, was too small to admit of sufficient purification for analysis.

Dinitro-benzyl-phenol.

If some mono-nitro-benzylphenol be dissolved in glacial acetic acid, and an equal bulk of concentrated nitric acid (free from nitrous vapours) be added, the whole warmed for a short time, and the liquid poured into water, a substance separates out on agitation in the crystalline form. After two or three crystallisations from alcohol, it has the constant melting point $87-88^{\circ}$. On analysis, the following numbers were obtained:—

0.1833 gram substance gave 15.26 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.01907 gram = 10.40 per cent.

Theory for $C_6H_5.CH_2.C_6H_2(OH)(NO_2)_2$ = 10.22 per cent.

The potassium-derivative, prepared in the usual way, crystallises from a hot solution in orange needles, and gave the following result after drying at 110° :—

0.1723 gram substance yielded 0.0482 gram K_2SO_4 = 0.021606 gram K = 12.54 per cent.

Theory for $C_6H_5.CH_2.C_6H_2(OK)(NO_2)_2$ = 12.50 per cent.

By substituting potassium nitro-benzyl-phenol-sulphonate (see this Journal, 1882, 35) for the mono-nitro-derivative, proceeding otherwise as above, the same body is obtained. A specimen prepared in this way melted at $87-88^{\circ}$, and gave the following numbers on analysis:—

0.136 gram substance yielded 11.1 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.01389 gram = 10.20 per cent.

Theory 10.22 per cent.

On oxidation with chromic liquor this body yields benzoic acid.

On treatment with concentrated nitric acid, either alone or in acetic acid solution, it yields the trinitro-derivative (described in Part I), easily recognised by its melting point and characteristic silky needles.

Oxidation of Trinitro-benzyl-phenol.

On boiling trinitro-benzyl-phenol or its potassium-derivative for an hour or two with chromic liquor and cooling the liquid, an acid separates out in almost colourless crystals. It melts at 238°. The melting point, together with the following analysis, show it to be pure paranitrobenzoic acid :—

0.151 gram substance gave 9.98 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.012475 gram N = 8.26 per cent.

Theory for $C_6H_4(NO_2)_3.COOH$ = 8.37 per cent.

Nitro-bromo-benzyl-phenol.

If potassium bromobenzyl-phenolsulphonate be added in small portions at a time in fine powder to dilute nitric acid (about 1 : 1) with constant agitation, a yellow body separates out in the solid form. On solution in alcohol and recrystallisation therefrom, it separates in very brilliant yellow crystalline scales, which under the microscope are seen to be canoe-shaped. It melts at 64—65°. The following are the results of analysis :—

0.2055 gram substance yielded 8.00 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.01 gram = 4.86 per cent.

Theory for $C_6H_5.CH_2.C_6H_4(OH)NO_2.Br$ = 4.55 per cent.

0.1115 gram substance yielded 0.0675 gram AgBr = 0.028723 gram Br = 25.76 per cent.

Theory for $C_6H_5.CH_2.C_6H_4(OH)NO_2.Br$ = 25.97 per cent.

The potassium-derivative prepared in the usual manner, crystallises from hot water in brilliant red scales, which, on drying at 100—110°, become deep crimson. Analysis gave numbers as follows :—

0.1256 gram substance gave 0.0308 gram K_2SO_4 = 0.013807 gram K = 10.99 per cent.

Theory for $C_6H_5.CH_2.C_6H_4(OK).NO_2.Br$ = 11.27 per cent.

If potassium nitrobenzyl-phenolsulphonate in fine powder be suspended in glacial acetic acid, 1 mol. of bromine added, and the whole warmed in the water-bath, finally adding a small quantity of water,

the solution becomes clear. On the addition of a large quantity of water, a yellow substance separates, which after crystallisation from alcohol melts at 64—65°. The crystals have the peculiar appearance described above as belonging to the body produced by the action of nitric acid on potassium bromobenzyl-phenolsulphonate. The potassium-derivative is also identical in appearance with that above described. Analysis gave the following result:—

0.2723 gram substance gave 0.0668 gram K_2SO_4 = 0.02995 gram

K = 10.99 per cent.

Theory 11.27 per cent.

There can be no doubt, therefore, that this body is identical with that produced by the action of nitric acid on potassium bromobenzylphenol-sulphonate.

If one molecular proportion of bromine be added to a solution of the mono-nitro-derivative in glacial acetic acid, and the liquid be poured into water, a substance separates, which is easily recognised by its melting point and crystalline form as the same nitro-bromo-derivative.

If one molecular proportion of bromine be added to a solution of benzyl-phenol in glacial acetic acid, and the liquid poured into water, an oil separates. This could not be obtained in the solid form, and has not yet been further examined, but on dissolving it in glacial acetic acid and nitrating in the usual way, it yields a body identical in all respects with the nitrobromo-derivative above described.

Thus whether the sulpho-group in the bromosulphonate be displaced by the nitro-group, or that in the nitrosulphonate by bromine, or whether benzyl-phenol itself be first brominated and then nitrated, or *vice versa*, the same body is obtained in every case.

Action of Nitric Acid on Nitrobromo-benzylphenol.

In the hope of obtaining a *di*-nitrobromo-derivative, some of the substance just described was dissolved in glacial acetic acid, somewhat more than an equal bulk of nitric acid added, and the whole warmed for some minutes. The reaction, however, took place in a very unexpected manner. On pouring the solution into water, a crystalline substance separated out, the melting point of which, after purification, proved to be 118°. Four different specimens all melted at or close to 118°. By slow cooling it separates from its alcoholic solution in very fine needles of a pale yellow colour. Analysis gave the following results:—

0.127 gram substance yielded 10.75 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.01344 gram = 10.58 per cent.

0.1434 gram substance yielded 11.89 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.01486 gram = 10.36 per cent.

0.1224 gram substance yielded 10.36 c.c. of nitrogen (reduced to 0° and 760 mm.) = 0.01295 gram = 10.66 per cent.

0.1803 gram substance yielded 0.1298 gram AgBr = 0.055236 gram Br = 30.63 per cent.

0.1176 gram substance yielded 0.0833 gram AgBr = 0.35447 gram Br = 30.14 per cent.

A combustion in oxygen with lead chromate gave the following numbers:—

0.1015 gram substance gave 0.1041 gram CO₂ = 27.97 per cent. C.

" " 0.0266 gram H₂O = 2.90 per cent. H.

These numbers agree well on the whole with those required for dinitrobromophenol. This will be better seen by the following comparison:—

	Found.						Calculated for C ₆ H ₂ (OH)(NO ₂) ₂ Br.
	I.	II.	III.	IV.	V.	VI.	
C....	27.97	—	—	—	—	—	27.38
H....	2.90*	—	—	—	—	—	1.14
N....	—	10.58	10.36	10.66	—	—	10.64
Br ..	—	—	—	—	30.63	30.14	30.42

The potassium-derivative was prepared as usual. It separated from a hot solution in golden-yellow needles, and gave on analysis the following result:—

0.1438 substance gave 0.0416 gram K₂SO₄ = 0.01862 gram K = 12.95 per cent.

Theory for C₆H₂(OK)(NO₂)₂Br = 12.95 per cent.

From its melting point, physical characteristics, analysis, and the appearance of its potassium-derivative, there can be little doubt that this body is *ortho-brom-α-dinitrophenol*, C₆H₂(OH)NO₂.NO₂.Br. (1 : 2 : 4 : 6 [OH] in 1). Its melting point is given by Körner as 118.2°.

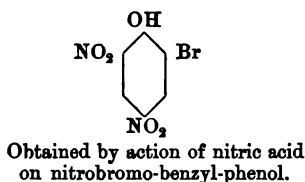
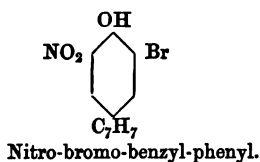
Its formation is important, as showing the constitution of the nitrobromo-derivative, and is the more peculiar because the dinitro-derivative, when treated in an exactly similar manner, yields not trinitro-phenol, but trinitro-benzyl-phenol.

* In this combustion a large quantity of red fumes were observed to pass into the sulphuric acid tube which happened to contain some chromic acid. This will account for the abnormal result. No more substance was available for a repetition of the combustion.

Constitution of Benzyl-phenol and its Derivatives.

The results thus obtained indicate pretty clearly the constitution of benzyl-phenol. The fact that the same nitrobromo-derivative is obtained whether nitric acid acts on the potassium bromosulphonate or bromine acts on the potassium nitrosulphonate, shows (admitting that no change takes place within the molecule) that the formula of this derivative, and consequently the formulæ of the bromosulphonate and of the nitro-sulphonate, *must be symmetrical*. This can be the case only if benzyl-phenol is a *para*-derivative.

Again, since nitrobromo-benzyl-phenol yields, by the action of nitric acid, as shown above, ortho-bromo- α -dinitrophenol, it follows that the substituting groups occupy the two ortho-positions relatively to the OH-group, and a confirmation of the view that the benzyl-group occupies the *para*-position is thus obtained. This will be apparent from the following formulæ:—



Since the dinitro-derivative is prepared by direct nitration of the nitrosulphonate, it would appear that in it also the two nitro-groups occupy the two ortho-positions, but it is in some respects anomalous. In the first place its melting point differs only by about 13° from that of the mononitro-derivative, while between the melting points of the corresponding *para*-cresol derivatives there is a difference of 40 — 41° . In the next place the yield, whether obtained from the mono-nitro-derivative or from the nitrosulphonate, is always very small. More important, however, is the abnormal colour of its potassium-derivative. As stated above, it yields *orange* needles; but the potassium compounds of di-ortho-nitro-derivatives of other phenols are characterised by the depth and beauty of their colour.

Again, one would expect that were the two nitro-groups in the two ortho-positions, it would yield trinitrophenol on treatment with nitric acid, since the nitrobromo-derivative yields the corresponding dinitro-bromophenol, but it yields instead trinitrobenzylphenol. Pending further investigation, therefore, the constitution of the dinitro-derivative must remain to some extent doubtful.

Since trinitro-benzyl-phenol is obtained by direct nitration from the dinitro-derivative, its constitution will depend upon that of the latter. One nitro-group, however, must occupy a position in the *benzyl*-group,

para to the CH₂-group, since it yields paranitrobenzoic acid on oxidation, while another must occupy the ortho-position relatively to the OH-group. The position of the third, for the reasons above stated, must be regarded as somewhat doubtful.

A direct proof that benzyl-phenol is a para-derivative is given in what follows.

Oxidation of Benzyl-phenyl-methyl Ether.

It was shown in Part I that by oxidation of this ether by alkaline permanganate, a neutral crystallisable substance is obtained easily soluble in alcohol and ether. It was there suggested that this is a ketone formed by oxidation of the methylene (CH_2) group. This view has been fully confirmed on further investigation. The substance forms large transparent four-sided prisms, which melt at $61-62^\circ$. Analysis gave the following results:—

0.1972 gram substance gave	0.5750 gram CO ₂ .
" " "	0.1056 " H ₂ O.
0.1495 gram substance gave	0.4350 gram CO ₂ .
" " "	0.0806 " H ₂ O.
0.1562 gram substance gave	0.4542 gram CO ₂ .
" " "	0.0824 " H ₂ O.

These numbers correspond to the following percentages :—

	Found.			Calculated for
	I.	II.	III.	$C_6H_5.CO.C_6H_4.O.CH_3$.
C	79.51	79.33	79.30	79.24
H	5.95	5.98	5.85	5.66

This body is, therefore, a *methoxybenzophenone*.

Some time since it was shown by Grucarevic and Merz (*Ber.*, 6, 1245) that by acting upon phenol with 1 mol. of benzoyl chloride, phenyl benzoate is produced, but that by using 2 mols. of the chloride with the further addition of zinc chloride, a benzoyl-phenyl benzoate, $C_6H_5.CO.C_6H_4.O.CO.C_6H_5$, is produced. On saponifying this compound with alcoholic potash they obtained potassic benzoate and a substance which they did not further examine.

This subject was taken up later on by Döbner (*Ber.*, 10, 1971), who investigated the body produced by the saponification, and showed, by an examination of its properties, and by obtaining from it paraoxybenzoic acid by fusion with potash at a low temperature, that it is *paraoxybenzophenone* or *parabenzoylphenol*, $C_6H_5.CO.C_6H_4(OH)$. It is evident that if benzyl-phenol be a *para*-derivative, the methyl ether of

paraoxybenzophenone must be identical with the body produced by oxidation of benzyl-phenyl-methyl ether.

In order to ascertain this point, some paraoxybenzophenone was prepared. After purification it melted at 134° , the temperature given by Döbner. Some of it was then mixed with the theoretical quantity of KHO (previously dissolved in alcohol) and a slight excess of methyl iodide, and the whole heated in a sealed tube for three or four hours to about 130° . The contents of the tube, after evaporating off the alcohol, &c., were treated with ether, the latter evaporated, and the crystalline substance which separated pressed and purified by recrystallisation. Thus prepared, it presented an appearance exactly similar to that of the oxidation-product above described. It melted at $61-62^{\circ}$. On combustion it yielded the following numbers:—

0.1624 gram substance gave 0.4730 gram CO_2 .
 „ „ „ 0.0866 „ H_2O .

These correspond to the following percentages:—

	Found.	Calculated for $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3$.
C.....	79.43	79.24
H	5.92	5.66

The two substances are, therefore, identical, and have the constitution of *paramethoxybenzophenone*. A direct proof is thus afforded of the constitution of benzyl-phenol, which is shown to be a para-derivative. I hope soon to be able to continue this investigation with a view to the preparation and examination of other derivatives.

ADDENDUM.

By the action of benzyl chloride on phenyl acetate, Perkin and Hodgkinson (this Journal, 1880, Trans., 724) obtained a benzyl-phenyl acetate, which on saponification yielded a benzyl-phenol. A small specimen of this substance (kindly placed at my disposal by Dr. Hodgkinson) was nitrated, and yielded a nitro-body, identical in appearance with the mono-nitro-derivative above described, and melting at 71° . The slight difference in melting point (3°) is doubtless due to slight impurity, the quantity of substance being too small to purify it very thoroughly. There is little doubt, therefore, that this body is also parabenzylphenol.

ANNIVERSARY MEETING.

March 30th, 1882.

Professor Roscoe, LL.D., V.P.R.S., President, in the Chair.

The following Report was read by the President:—

In again reporting on behalf of the Council respecting the present condition of the Society, I have the honour to remark that the number of Fellows is larger than it has ever been, for now 1,175 names are enrolled on the register of the Society, as against 1,115 on the 30th of March last, no fewer than 95 new Fellows having been elected, and having paid their admission fees during the past financial year.

The number of original communications made to the Society during the past session has been 87; this is somewhat fewer than the numbers I announced last year, but it is larger than in any other previous session of the Society's existence, and the material has certainly not fallen below the average, either in interest or importance.

To Professor Odling the Society is indebted for his lucid discourse on the "Unit Weight and Mode of Constitution of Compounds," delivered on February 2.

The financial condition of the Society continues satisfactory, as seen in the Treasurer's report, the balance to the credit of the Society being now £1,422. 5s. 5d., as against £1,205 2s. 2d. last year, whilst during the past year the sum of £300 has been invested.

The most noteworthy feature connected with the action of our Society during the year now closing, has been the delivery by Professor Helmholtz of the Faraday Lecture, on April 5th. The subject chosen by this distinguished physicist was one appropriate to the occasion, viz., "On the Modern Development of Faraday's Conception of Electricity," and it was as a matter of course treated with the lucidity and completeness characteristic of all Helmholtz's work. Specially interesting to chemists is the discussion of the fundamental problem aimed at by Faraday, viz., the connection between electric and chemical force, showing in the first place that Berzelius' electrochemical theory, viz., that the quantity of electricity collected at the point of union of two atoms increases with the strength of their affinity, was proved to be incorrect by Faraday's discovery of the law of definite electrolytic action. Helmholtz proceeds to point out that, according to the modern

theory of valency, the same quantity of electricity passing through an electrolyte either sets free, or transfers to other combinations, always the same number of units of affinity at both electrodes.

The Faraday Lecturer, however, goes further, and argues that if we accept the hypothesis that elementary substances are composed of atoms, we cannot avoid the conclusion that electricity also, both positive and negative, is divided into elementary portions, which behave like atoms of electricity. Each chemical atom is accompanied by its electrical equivalent, hydrogen of negative and oxygen of positive electricity, and these electrical atoms are given off at the electrode only when a sufficient amount of electromotive force is present. He then shows that the charges of electricity accompanying the atom are enormously large in comparison with the amount of chemical decomposition effected, and as an illustration of this, he asserts that the polarization produced in a few seconds on two platinum wires can readily be observed with a current which would decompose only 1 milligram of water in a century. Or, to put the same result in another form, that the attraction between the electric charges of the atoms of oxygen and hydrogen is 71,000 billion times greater than the attraction of gravitation between the same atoms.

Helmholtz thus accounts for the difficulty which has been experienced in obtaining even indications of electrolytic decomposition in many cases in which non-conductors become electrically charged, and he proves the fact that such decomposition does occur, by a very ingenious arrangement of a Daniell's element, having the porous cell replaced by a thin stratum of glass, and with this apparatus the electromotor can be charged. This would not be the case if the stratum of glass did not behave like an electrolyte.

The Society will, I feel sure, desire that its Council should, in its annual report, again formally thank Professor Helmholtz for the honour he has conferred upon the Society by the delivery and publication of the Faraday Lecture.

With regard to the progress of chemical science during the past year, I may perhaps be allowed to say a few words, and I would in the first place remind you that the subjects of the advancement of chemical industry and the encouragement of technical scientific instruction in this country are matters upon which our Society cannot but look with interest. The establishment, therefore, of a Society of Chemical Industry, which is intended to bring into closer union all the scattered branches of manufacture and trade dependent on chemical principles, must be a matter of congratulation, as assisting our efforts in a more purely scientific direction. The two Societies will, it is to be hoped, prove of mutual advantage.

The monthly Journal of the new Society will also supplement our

own, as giving the most important applications of our science to the numerous branches of national industries.

In another direction, also, I feel glad to be able to report progress. The subject of technical scientific instruction is one which has for some years been prominently before the public, and the question as to the position occupied by our own country in this respect as compared with others, especially continental countries, has been made the subject of lively discussion.

During the last session of Parliament the Government was pressed on more than one occasion to appoint a commission for the purpose of investigating the whole subject of technical instruction, more especially with reference to what has been recently done in this direction on the Continent. Early in July last Mr. Mundella was able to announce in the House of Commons, in reply to Mr. Macdonald, that he believed that "without putting the country to the expense of a roving commission throughout Europe, the necessary information could be obtained." Subsequently, on the 26th of August, the appointment was gazetted of a royal commission, consisting of the following members:—B. Samuelson, Esq., M.P., F.R.S. (chairman); H. E. Roscoe, Esq., LL.D., F.R.S., Philip Magnus, Esq., B.A., B.Sc.; John Slagg, Esq., M.P., Swire Smith, Esq., and William Woodall, Esq., M.P., with Mr. Gilbert R. Redgrave, of the Science and Art Department, as secretary. In accepting this appointment, I felt that I should be acting in accordance with the best interests of the Society, and in furtherance of chemical education, although I was obliged to absent myself from several of your meetings. The warrant of appointment defines the object of the commission as follows:—"To inquire into the instruction of the industrial classes of certain foreign countries in technical and other subjects, for the purpose of comparison with that of the corresponding classes in this country, and into the influence of such instruction on manufacturing and other industries at home and abroad." Before visiting the Continent, the commissioners inspected a few of the chief manufactories in Yorkshire engaged in the woollen trade, and the technical schools of Leeds, Bradford, and Keighley. They also went through some of the principal works in the Potteries, and examined the various processes of silk manufacture at Leek and Macclesfield. The first place on the Continent to which they directed their inquiries was Milan, in order to have the opportunity of seeing the exhibition in that city before it closed, on the 31st of October. While in the north of Italy a few visits were paid to silk and woollen manufactories, and to certain typical schools in Milan, Turin, Como, and Biella. On leaving Italy, the commissioners met in Paris, on the 2nd of November, and devoted a month to the careful examination of the national schools of arts and trades, the *Ecole*

Centrale, Ecole des Mines, Conservatoire des Arts et Métiers, and principal art schools and night classes. I need scarcely add that I took occasion to inform myself concerning the opportunities offered in France for both theoretical and practical instruction in chemical science, from the lowest to the highest stages, and a full account of these matters will appear in the reports which the Commissioners will from time to time publish. On leaving Paris, some of the principal manufacturing towns of France were selected, and the educational facilities offered in each to the industrial classes were carefully studied. Thus, Lyons, Rheims, Lille, Roubaix, Rouen, Limoges, Nismes, Toulouse, and Amiens were in turn visited, and in each of the towns the members of the commission endeavoured by visits to leading manufactories and by consulting the local authorities, to ascertain how far the schools and institutions were exerting a beneficial influence upon the trade of the district. It is the intention of the Commissioners to visit Belgium and Germany in the spring. In order to make themselves fully acquainted with what is being done in our own country, the Commissioners have already devoted some time to the inspection of some of the manufacturing towns in this country. Thus they have visited or are about to visit Manchester, Liverpool, Birmingham, Sheffield, Oldham, Nottingham, and Glasgow, in order to study the excellent educational advantages offered by these towns, for the purpose of comparison with similar institutions abroad. The Commissioners have issued a brief report on primary instruction in France, and the new laws which came into operation in that country on the 1st of January last, reserving for subsequent publication their views upon the higher scientific education both at home and abroad.

I have likewise to report that I have attended the meetings of the Council of the City and Guilds of London Institute, and that I have also been consulted upon the arrangements of the new Central Technical College, now building at South Kensington.

Amongst the many important advances made during the year in our science, I venture to refer only to the following, as indicating some of the directions in which progress is being made.

In the first place, the no less interesting than important question of the variation in density which the halogens exhibit at high temperatures has, during the past year, been made the subject of experiment by several chemists. Crafts and Meier, in repeating the experiments of V. and C. Meyer by a somewhat different method, have shown that, whilst the dissociation of the molecule of iodine proceeds progressively from a little below 600° to the highest temperature attainable (when the density becomes very nearly one-half the normal value), the same increase of temperature affects gaseous chlorine to an inappreciable extent only. Victor Meyer and Zublin, in going over this ground

again, have confirmed the above conclusions. The result then appears to be that the molecules of gaseous chlorine are not dissociated at 1200° , but that if nascent chlorine, evolved from platinous chloride, be operated upon at the same temperature, a diminution to $\frac{2}{3}$ Cl_2 takes place, the occurrence of this constant value being explained by the fact that 2 mols. of chlorine (4 vols.) are dissociated into 1 mol., occupying 2 vols. and 2 semi-molecules, each occupying the same bulk of 2 vols. The one modification of chlorine bears therefore to the other, the same relation as regards density that oxygen bears to ozone. The case of bromine would seem to be identical with that of chlorine. At 157° bromine evolved from platinous bromide exhibits a density of $\frac{2}{3}$ Br_2 . The density of free bromine at high temperatures has not yet been ascertained with exactitude, owing to experimental difficulties.

In discussing the above results, several different explanations have been given, some believing that variations at high temperatures in the laws of Dalton, Charles, and Boyle are sufficient to explain the observations without recourse to the assumption of molecular dissociation. It is to be remembered, however, that, in the case of iodine at least, the differences observed between the channelled space spectrum of iodine at low temperatures and that of the line spectrum of iodine at high temperatures, point rather to a variation in the molecular condition of this element.

Another interesting case of change of density and molecular weight with change of temperature has recently been observed by Mallet in hydrofluoric acid gas. This exhibits at 30° a density corresponding to the formula H_2F_2 , whilst at 100° its density is found to be one-half of this, or the molecule at this temperature is represented by HF .

As indicating progress in Mineral Chemistry, the experiments of Setterberg on the preparation of caesium metal and the caesium salts deserve a word of notice. He has been fortunate enough to obtain the salts of rubidium and caesium in very large quantities, and has made use of a very simple reaction for their separation. The alum of each of these new metals and also that of potassium, is insoluble in a saturated solution of the others. Thus a mixture of caesium and rubidium alum is thrown completely out of solution by one of potassium alum, whilst the caesium salt is precipitated from a solution of rubidium alum.

Having thus obtained 40 kilos. of pure rubidium alum and 10 kilos. of pure caesium alum, he proceeds to repeat Bunsen's well-known experiment on the preparation of metallic caesium by the ordinary carbon-reduction process, and perhaps no greater proof of the accuracy of this great master's work can be mentioned than the fact that Setterberg, with his kilograms of caesium salt, confirmed Bunsen's observations made on as many centigrams, that no metallic caesium

can be thus obtained. However, he succeeded in obtaining the metal by electrolysis of the cyanide, and finds that it melts at 26.5° , and possesses a specific gravity of 1.88.

Mention should also be made of the recent researches on the cerite metals by Dr. Brauner, and communicated to the Society. These are of interest as pointing out the true position of cerium and didymium in the periodic system; in the one case by the isolation of the tetrafluoride, and on the other, by that of the pentoxide.

The existence of yttrium for the first time in a British mineral has also been announced to the Society by Professor Hartley in a paper containing other interesting results.

Turning to the more widely cultivated fields of Organic Chemistry, one fortunately feels absolved from quotation by the very immensity of the area of selection, and three references having bearing on what I stated in the last report must suffice.

In the first place, Perkin's investigation of the derivatives of coumarin communicated to the Society, has brought to light several interesting cases of isomerism, from the study of which a clue to the long disputed question of the constitution of fumaric and maleic acids has been obtained.

Secondly, Baeyer's researches on the indigo-group have been continued during the past year with conspicuous success. He has occupied himself chiefly with an endeavour to explain the molecular changes which occur in the reducing actions taking place when ortho-nitrophenylpropionic acid is treated with grape-sugar, and he has shown that this depends on the formation of an intermediate product, *indoxyl*, C_8H_7NO , which by the condensation of 2 mols. yields indigo-white, and then indigotin.

In the third place, Ladenburg in continuing his researches on atropine, has, during the past year, devoted himself to the study of the constitution of tropine, which he has shown to be a tertiary base. He has also proved that tropine belongs to a class of compounds termed by him *alkines*, which, in virtue of the presence of an alcoholic hydroxyl, form ethereal salts or *alkeines*, atropine being the alkeine of tropic acid. Respecting the constitution of tropine, he has, however, as yet obtained but little further information; but it may be well to notice that in the elucidation of this important problem, both Ladenburg and Merling, who is likewise working in the same direction, have employed the reaction discovered by Hofmann, viz., the decomposition by heat of the substituted ammonium hydroxides, which, in the cases of conine and piperidine, has, in Hofmann's hands, thrown light on the constitution of these bases. In this connection I must not fail to mention the important facts of the artificial production of caffeine from xanthine by E. Fischer, and of the structural connection

of piperidine and nicotine made out by Otto Fischer, Schotten, and Königs.

Since the last Anniversary Meeting, the Society has lost 11 Fellows and two foreign members—Professor Etienne Henri Sainte-Claire Deville and M. Victor Dessaignes.

The deceased Fellows are:—A. E. Arnold; F. J. Barrett; Edward Buckney; R. C. Clapham; R. Gersth; John Mackay; A. Freire-Mareco; R. W. Thomas; J. S. Walton; Arthur Willis; and H. J. Zeld.

In the death of HENRI SAINTE-CLAIRE DEVILLE the Society has lost one of its most brilliant foreign members, and the world of science one of the most gifted men of the time.

Deville, in common with so many of the present generation of French chemists, owed his first introduction to this enthusiasm for the science to Dumas. In 1851 he succeeded Balard in the Chair of Chemistry at the Ecole Normale. To this school he remained devotedly attached all his life, and his laboratory soon became, and remained, until his death, one of the chief centres of chemical activity, not only in Paris, but in Europe. To enumerate even the more remarkable researches of Deville would here be out of place. It may perhaps be sufficient to remind the Society that the earliest notable achievement of our late foreign member was the isolation in 1849 of nitrogen pentoxide; that upon that followed his memorable work on aluminium, of world-wide renown; and here it is interesting to remember, as a subsidiary result of this investigation, and one which has been of the greatest service to chemists, the fact that the aluminium research caused a reduction in the price of sodium from about £40 to 5s. per lb.

The history of his researches on the platinum metals, chiefly undertaken with his friend and successor Débray, will be in the minds of the Fellows, and our Society may congratulate itself that in a portion, and not the least important portion, of these investigations, Deville was aided in his preparation of large masses of the pure metals and their alloys by the sound knowledge and manipulative skill of Mr. George Matthey. Nor must we forget that these researches were accompanied with danger to life, and that Deville on more than one occasion suffered severely from the poisonous effect of the vapours of osmic acid.

Facility having been obtained for working at high temperatures, Deville was led to study the artificial production of crystalline minerals, such as zircon, topaz, periclase, &c., and his success in this direction gave the first impetus to the artificial manufacture of crystalline minerals, which has now become general.

But it is especially in two other directions that Deville's researches in Thermal Chemistry have been productive of such marked results; that in one case at least an entirely new and, as it has subsequently proved, most fruitful field of investigation was opened out. I need scarcely say that I allude, in the first place, to his researches on vapour-density determinations at high temperatures, made chiefly together with Troost, and secondly, to the discovery of the phenomena of dissociation, and of the laws which underlie those phenomena, discoveries with which the name of Deville will for ever be inseparably connected.

Although he held himself aloof from discussions, especially on points of theoretical interest connected with our Science, few men have done more than Deville to widen the boundaries of chemical knowledge, and it will be a lasting honour to our Society that the name of this eminent chemist so long adorned our list of foreign members.

The name of VICTOR DESSAIGNES is perhaps less generally known to the younger Fellows than that of our deceased colleague Deville; but when we remember his discovery of malonic acid, and his researches on hippuric acid and glycocholl, on the formation of succinic acid by oxidation of butyric acid, and of many other investigations of a like importance, we shall all acknowledge that when Dessaignes died at the ripe age of 82, our Science lost a veteran who had fought a good fight in a day when the present generation of chemists was not.

Amongst our home losses I have to note that of Mr. ARTHUR EDWARD ARNOLD, who was born at Midhurst, Fortis Green, Finchley, 2nd September, 1857, and died at Leghorn, 24th September, 1881, of consumption. He was analytical chemist to Messrs. Hollway of St. Mary Axe, and Associate (by examination) of the Society. Mr. Arnold was a young man of much promise, and a true lover of science for its own sake.

In Mr. CALVERT CLAPHAM, of Earsden House, near Newcastle-on-Tyne, the Society has lost a Fellow well-known amongst technical chemists.

Mr. Clapham, who was elected on March 19th, 1868, died suddenly whilst on a visit to Winchelsea, from heart disease, on the 22nd December, 1881, aged 58 years. He was born at Benwell Grove, near Newcastle, in 1823, and was the son of Anthony Clapham, proprietor of the second oldest chemical works on the Tyne. He received his education from a private tutor, and afterwards at Durham, and gained his first experience in chemical works at his father's works, where he re-

mained till about 1844. He then undertook the management of chemical works at Ardrossan, and subsequently, in 1858, he became manager of the Walker Alkali Works, the oldest established alkali works on the Tyne. He held this post up to about ten years ago, when he retired from business, but he still engaged himself actively as a director of various companies.

Mr. Clapham did much to further the development of science in his own town by the energetic interest he took in local scientific societies. He was for the last 21 years Secretary of the Newcastle-on-Tyne Literary and Philosophical Society, and may be considered, if not the founder, one of the first and chief promoters of the Newcastle Chemical Society, formed in 1868, of which he was President for two years, in 1878 and 1879. He was the author of several papers communicated to the above society, on subjects connected with the chemical industry of the district. Mr. Clapham also contributed papers on chemical and geological subjects to the *Chemical News*, the *Geologist*, and other scientific journals. He was one of the local secretaries at the Newcastle meeting of the British Association in 1863, and, together with the late Dr. Thomas Richardson and J. C. Stephenson, Esq., M.P., compiled the Report on the Chemical Manufactures of the Newcastle District, which was prepared for that meeting.

In 1875 Mr. Clapham was appointed Examiner on the Alkali Manufacturers in the Technological Examination of the Society of Arts, and continued as examiner when the City and Guilds of London Institute took over the technological examinations of the Society.

Mr. RUDOLF GEESTL came to this country from Buda-Pest about the year 1868, and was for a time occupied in the laboratory of St. Thomas' Hospital. Thence he went to University College, and was employed by Dr. Williamson and Dr. Burdon-Sanderson, and afterwards appointed a Master in University College School. He re-wrote the article on "Chlorine" in the new edition of *Muspratt's Chemistry*, and devoted much time to devising lecture-experiments and other means of making the elements of science clear to the beginner. He was for many years an examiner in chemistry and physics at the Royal Military Academy, Woolwich; and for a still longer time the English correspondent of the German Chemical Society. He died on July 23rd, 1881, in the 36th year of his age.

Mr. JOHN MACKAY, a well known pharmacist in Edinburgh, was born in that city in 1818. In after life he served on the Council of the Pharmaceutical Society, where his advice was much valued. He contributed several papers to the Royal Scottish Society of Arts, for one of which, in connection with German yeast, he received the Society's

silver medal. He was elected a Fellow of the Society on April 4th, 1867.

The name of Mr. W. R. THOMAS will long be remembered by photographers as the manufacturer of the excellent collodion which bears his name, and to the preparation of which he devoted much care and attention. He published several papers on subjects connected with practical photography, which will be found in vols. v, vi, vii (old series), of the *Journal of the Photographic Society of Great Britain*. He was elected a Fellow on June 21st, 1877.

Professor A. FREIRE-MARRECO was born in North Shields in 1836, but appears to have received his earlier scholastic training in Portugal, the native country of his father. He returned to England while still a youth, and subsequently entered the chemical laboratory of Dr. Thomas Richardson, the joint author of *Chemical Technology*. Here he soon became a trusted assistant, and in 1859, Dr. Richardson appointed the young chemist his deputy in the office of Reader in Chemistry in the University of Durham, and Lecturer in Chemistry and Demonstrator in Practical Chemistry in the Newcastle School of Medicine. Eight years afterwards, Mr. Marreco, who had meanwhile become Dr. Richardson's partner, succeeded to those offices.

In 1871, the Newcastle College of Science was founded, and Mr. Marreco, notwithstanding that his prospects as a consulting analyst were now very promising, became a candidate for the chair of Chemistry in that institution, and received the appointment. As a professor he strove to realise a very high ideal, believing that one holding such a position should give himself up entirely to his teaching, and it is stated that accordingly he never, from the day of his appointment, accepted remuneration for any work unconnected with the college curriculum.

Professor Marreco does not appear to have written very much, but a communication giving the results of a series of experiments on coal-dust explosions, published in the *Transactions of the North of England Institute of Mining Engineers*, forms one of the earliest as well as most valuable contributions to the history of the subject.

Professor Marreco took an active part in the management of various scientific societies. He assisted to found the Newcastle Chemical Society, which he then served first as Secretary and afterwards as President. He was also a member of the first Council of the Institute of Chemistry.

Mr. JONATHAN SPARKE WALTON died March 6th, 1881, aged 34. He became a Fellow of the Society on March 16th, 1876.

Mr. ARTHUR WILLIS, who died in April, 1881, was the son of Professor Willis, of Cambridge. He received his scientific training at the Royal School of Mines, where he studied under Professor Frankland and Dr. Percy. After passing through the usual course of study in that institution, he received the appointment of chemist in the Sample Steel Works in Birmingham, under the direction of Dr. C. W. Siemens. When there he carried out all the chemical work connected with the open Hearth Regenerative Steel furnace, which was first started in these experimental works. In the year 1869, when the Landore-Siemens Steel Company was started, Mr. Willis received the appointment of chemist, and remained connected with this Company till his death. His great knowledge of Analytical Chemistry, more especially as applied to the analysis of iron and steel, enabled him to devise many methods for facilitating that portion of the work in his laboratory, and had his life been spared, it was his intention to publish them. Mr. Willis communicated several papers to the Iron and Steel Institute on the Chemistry of Steel-making. He was very popular with all who knew him.

Titles of Papers read since March 30, 1881.

- I. "On Organic Matter in Sea-water:" by W. Jago.
- II. "On the Action of Compounds inimical to Bacterial Life:" by W. M. Hamlet.
- III. "On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride:" by F. D. Brown.
- IV. "On the Estimation of Hydrogen Peroxide by Means of Potassic Permanganate:" by W. E. Adeney.
- V. "On the Oxidation of Sulphurous Acid:" by H. B. Dixon.
- VI. "On the Reduction of Cinnylic Alcohol:" by F. Hatton and W. R. Hodgkinson.
- VII. "On the Action of Humic Acid upon Atmospheric Nitrogen:" by E. W. Prévost.
- VIII. "On the Active and Inactive Amylamines:" by R. T. Plimpton.
- IX. "On the Action of Sodium Alcoholates on Fumaric Ethers:" by T. Purdie.
- X. "On the Products of the Action of Alkalis on Ethylic β -ethyl-acetosuccinate:" by L. T. Thorne.
- XI. "On Some Carbazol-compounds:" by E. H. Rennie and W. K. Hodgkinson.
- XII. "On Ammonium Nitrate and the Reaction between Hydrogen

- and Nitric Oxide in presence of Spongy Platinum:" by L. T. Wright.
- XIII. "On the Synthetical Production of Urea from Benzene, Ammonia, and Air, by the Action of Heated Platinum:" by E. F. Herroun.
- XIV. "On a Proposed Volumetric Method for the Ready Estimation of a Soluble Sulphite and free Sulphurous Acid, or of free Sulphurous and Sulphuric Acids, even in the presence of Sulphates:" by O. V. Pisani.
- XV. "On the Identification of Crystallised Alkaloids, &c., by the Microscope, and the Use of Polarised Light:" by A. Percy Smith.
- XVI. "On the Colour-properties and (Colour-reactions of the Metals of the Iron and Copper Group:" by T. Bayley.
- XVII. "On the Effects of the Growth of Plants on the Amount of Matter removed from the Soil by Rain:" by E. W. Prévost.
- XVIII. "On the Action of Sodium on Cinnamic Ether:" by F. Hatton.
- XIX. "Experimental Researches on the Amalgamation of Silver Ores:" by C. Rammelsberg.
- XX. "On the Action of Solvents on Saponified Oils and Waxes:" by W. A. Allen and W. Thomson.
- XXI. "On the Sulphides of Copper, and a Determination of their Molecular Weight:" by S. W. Pickering.
- XXII. "Chemical Examination of the Buxton Thermal Water:" by J. C. Thresh.
- XXIII. "On Potable Waters. (Part II.) Determination of Total Solids:" by E. J. Mills.
- XXIV. "On the Estimation of the Value of Zinc Powder, and on a Gauge for Measuring the Volume of Gases without Calculation for Temperature and Pressure:" by J. Barnes.
- XXV. "On the Isomeric Acids obtained from Coumarin, and the Ethers of Salicylic Aldehyde:" by W. H. Perkin.
- XXVI. "Notes on Naphthalene Derivatives:" by H. E. Armstrong and C. Graham.
- XXVII. "On the Synthesis of Ammonia:" by G. S. Johnson.
- XXVIII. "On the Alkaloids of Nux Vomica:" by W. A. Shennstone.
- XXIX. "Researches on the Relation of the Molecular Structure of Carbon Compounds to their Absorption-spectra:" by W. N. Hartley.
- XXX. "On the Sulphates of Aluminium:" by S. W. Pickering.
- XXXI. "On Two New Oxides of Bismuth:" by M. M. P. Pickering.

- XXXII. "Modified Form of Apparatus for Collecting the Gases Dissolved in Water:" by J. C. Thresh.
- XXXIII. "On the Synthesis of α -Isoheptane:" by Thomas Purdie.
- XXXIV. "On a New Derivative of Quinine:" by E. H. Rennie.
- XXXV. "Metallic Compounds containing Bivalent Hydrocarbon Radicals." Part II: by J. Sakurai.
- XXXVI. "Note on the Formation of an Alcoholic Fluoride:" by Sydney Young.
- XXXVII. "Contributions to the History of the Mineral Waters of Yorkshire:" by T. E. Thorpe.
- XXXVIII. "Fractional Distillation with a Still-head of Uniform Temperature:" by F. D. Brown.
- XXXIX. "On the Action of Oxides on Salts. (Part III):" by E. J. Mills and C. W. Meanwell.
- XL. "On the Action of Tertiary Amines upon Acetylene Dibromide:" by R. T. Plimpton.
- XLI. "Suberone:" by R. S. Dale and C. Schorlemmer.
- XLII. "On Dimethylmalonic Acid and Dimethylbarbituric Acid:" by L. T. Thorne.
- XLIII. "On Phenyl-naphthalen:" by Watson Smith and T. Takamatsu.
- XLIV. "Sulphonic Acids derived from Isodinaphthyl ($\beta\beta$ -Dinaphthyl):" by Watson Smith and T. Takamatsu.
- XLV. "On Citraconic and Mesaconic Ethers, and Maleic and Fumaric Acids:" by W. H. Perkin.
- XLVI. "On the Atomic Weight of Bismuth:" by M. M. P. Muir.
- XLVII. "Note on the Action of Sulphuric Acid on Zinc and Tin:" by M. M. P. Muir and C. E. Robbs.
- XLVIII. "On the Volumetric Estimation of Bismuth in the Form of Oxalate:" by M. M. P. Muir and C. E. Robbs.
- XLIX. "Note on the Influence of Water on the Reaction between Potassium Iodide and Chlorine:" by M. M. P. Muir and R. Threlfall.
- L. "Laboratory Notes:" by M. M. P. Muir.
- LI. "Aluminium Alcohols (Part II); their Products of Decomposition by Heat:" by J. H. Gladstone and A. Tribe.
- LII. "On the Combustion of Pennant Grits in contact with, and at a distance from, Carbonaceous Deposits:" by A. Wethered.
- LXIII. "On α - and β -Amylan:" by C. O'Sullivan.
- LIV. "On the Action of Oxides on Salts (Part IV). Potassic Chlorate and Ferric Oxide:" by E. J. Mills and G. Donald.
- LV. "On the Steeping of Barley:" by E. J. Mills and J. Pettigrew.
- LVI. "Researches on the Laws of Substitution in the Naphthalene Series. (Part II):" by H. E. Armstrong.

- LVII. "On Benzylphenol and its Derivatives:" by E. H. Rennie.
- LVIII. "Note on the Action of Ethyl Chlorocarbonate on Benzene in the Presence of Aluminium Chloride:" by E. H. Rennie.
- LIX. "On the Production of Oxalic Acid by Oxidation of Paraffin Oil:" by J. Galletly and J. S. Thomsen.
- LX. "On some Higher Oxides of Manganese and their Hydrates:" by V. H. Veley.
- LXI. "On a New Alkaloid from Cinchona Bark:" by D. Howard and J. Hodgkin.
- LXII. "Contributions to the Chemistry of the Rare Earth-metals:" by B. Brauner.
- LXIII. "The Chemistry of Bast Fibres:" by C. F. Cross and E. J. Bevan.
- LXIV. "A New Apparatus for Determining Fusing Points:" by C. F. Cross and E. J. Bevan.
- LXV. "On the Action of Heat on Mercuric Chloride under Low Pressures:" by T. Carnelley.
- LXVI. "Contributions to the History of the Cerium Compounds:" by W. N. Hartley.
- LXVII. "On the Reaction of Chromic Anhydride with Sulphuric Acid:" by C. F. Cross and A. Higgin.
- LXVIII. "On Dibenzylaniline and its Isomerides:" by A. Higgin.
- LXIX. "On Benzyl-phenol and its Derivatives" (Part II): by E. H. Rennie.
- LXX. "On Retrograde Phosphates:" by F. Lloyd.
- LXXI. "Contribution to our Knowledge of the Composition of Alloys and Metal Work, for the most part Ancient:" by W. Flight.
- LXXII. "On the Dissociation of Chlorine:" by A. P. Smith and W. B. Lowe.
- LXXIII. "On Peppermint Camphor (Menthol) and some of its Derivatives:" by R. W. Atkinson and H. Yosida.
- LXXIV. "Note on Certain Photographs of the Ultra-violet Spectra of Elementary Bodies:" by W. N. Hartley.
- LXXV. "On Some Decompositions produced by the Action of Chloride of Aluminium:" by C. Friedel and J. M. Crafts.
- LXXVI. "On the Action of Aldehydes on Phenanthraquinone in Presence of Ammonia" (3rd Notice): by F. R. Japp and F. W. Streatfield.
- LXXVII. "Application of the Aldehyde and Ammonia Reaction in Determining the Constitution of Quinones:" by F. R. Japp and F. W. Streatfield.
- LXXVIII. "On the Solubility of Glass in Certain Reagents:" By R. Cowper.

LXXIX. "Analysis of a Piece of Oxidised Iron from the Condenser of H.M.S. 'Spartan':" by R. Cowper.

LXXX. "On the Action of Sodium Hydrate and Carbonate on Felspars and Wollastonite:" by W. Flight.

LXXXI. "On the Preparation of Pure Nitrogen:" by W. Flight.

LXXXII. "Some Observations on the Luminous Incomplete Combustion of Ether and other Inorganic Substances:" by W. H. Perkin.

LXXXIII. "On Valency:" by H. E. Armstrong.

LXXXIV. "On Pentathionic Acid:" by Watson Smith and T. Takamatsu.

LXXXV. "On Some Constituents of Resin Spirit:" by G. H. Morris.

LXXXVI. "On the Preparation of Diethylnaphthylamine, and the Action of Sulphuric Acid on that Substance:" by B. Smith.

LXXXVII. "Contributions to the Chemical History of the Aromatic Derivatives:" by R. Meldola.

Dr. Odling delivered a Lecture on the Unit Weight and Mode of Constitution of Compounds.

The following Officers were then announced from the chair as having been duly elected for the ensuing year:—

President.—J. H. Gilbert, Ph.D., F.R.S.

Vice-Presidents who have filled the Office of President.—F. A. Abel, C.B., F.R.S.; Warren de La Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; W. Odling, M.B., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; Henry E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents.—A. Crum-Brown, D.Sc., M.D.; J. Dewar, F.R.S.; Peter Griess, Ph.D., F.R.S.; A. V. Harcourt, F.R.S.; J. E. Reynolds, M.D., F.R.S.; E. Schunck, Ph.D.

Secretaries.—W. H. Perkin, F.R.S.; H. E. Armstrong, Ph.D., F.R.S.

Foreign Secretary.—H. Müller, Ph.D., F.R.S.

Treasurer.—W. J. Russell, Ph.D., F.R.S.

The other Members of the Council are—Capt. W. de W. Abney, R.E., F.R.S.; E. Atkinson, Ph.D.; F. D. Brown, B.Sc.; F. R. Japp, M.A., Ph.D.; H. McLeod; G. H. Makins; E. J. Mills, D.Sc., F.R.S.; C. O'Sullivan; C. Schorlemmer, Ph.D., F.R.S.; J. M. Thomson; W. Thorp, B.Sc.; T. E. Thorpe, Ph.D., F.R.S.

RESEARCH FUND.

DURING the past year, the following grants from the Research Fund have been made by the Council, on the recommendation of the Committee.

£50 to Prof. Thorpe for the redetermination of the Atomic Weight of Titanium and the examination of Titanium minerals.

£20 to Dr. Hodgkinson for the examination of derivatives of Acenaphthene.

£10 to Mr. E. H. Rennie for the investigation of Benzylphenol.

The Committee state that they have received reports from several gentlemen to whom grants have been made.

ANNIVERSARY MEETING.

245

	£	s.	d.	£	s.	d.	£	s.	d.
Balance at Bank March 23rd, 1881	1,204	18	2						
" in hands of Treasurer	0	4	0						
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 21st, 1881, to March 24th, 1882.									
13 Life Compositions	260	0	0						
101 Admission Fees	404	0	0						
9 Subscriptions for 1879	18	0	0						
47 " " 1880	92	0	0						
226 " " 1881	440	0	6						
609 " " 1882	1,180	0	6						
1 " " 1883	2	0	0						
Sale of Journal	334	17	6						
" Index	1	1	0						
Subscriptions for Proceedings of Royal Society from Institute of Chemistry	6	0	0						
" " Society of Public Analysis	4	0	0						
Dividends on Consols	117	10	0						
Metropolitan Board of Works	83	0	8						
London and North Western Railway	30	16	6						
Debenture Stock									
Assets.									
Balance at Bank	1,420	8	10						
In Treasurer's hands	1	16	7						
Three per Cent. Consols	4,000	0	0						
London and North Western Railway									
Debenture Stock	788	0	0						
Metropolitan Board of Works 3½ per cent. Stock	2,500	0	0						
Expenses on Account of Journal.									
Salary of the Editor	250	0	0						
Fees to Subscribers	100	0	0						
Incidental expenses of Editor	279	9	2						
Periodicals for use of Abstractors	4	10	0						
Distribution of Journal	34	5	9						
Printing of Journal	196	15	8						
	868	11	6						
Expenses on Account of Library.									
Salary of Librarian	50	0	0						
" Library Attendant	62	0	0						
Books and Periodicals	88	4	1						
Binding Books	33	0	10						
Printing Authors' Copies									
Proceedings of Royal Society, and Distributing same	31	1	2						
Reports of Meetings	64	11	8						
Miscellaneous Printing	24	0	0						
Insurance of Furniture and Books	41	14	0						
Inhabited House and Income-tax	2	0	0						
Stationery, Postage, &c.	6	17	6						
Collector's Commission on Subscriptions	28	13	4						
Treasurer's Stamps, Cheque Book, and Clerical Aid	119	16	0						
	5	0	10						
Expenses in connection with Faraday Lecture.									
Printing, Postage, and expenses at Royal Institution	10	12	6						
Preparation of Medal and Case	2	0	0						
Honorarium to Lecturer	20	0	0						
	32	12	6						
House Expenses.									
Providing Refreshments at Meetings	23	6	6						
Heating the Building	11	19	6						
Lighting	46	13	8						
Cleaning	20	0	0						
Wages of House Porter	50	12	0						
Petty House Expenses	7	18	6						
Repairing Gas Fittings	2	14	6						
Gratuity to Gate Porter	2	2	0						
Trying and Cleaning Fire Hose (2 years)	3	16	6						
Treasurer's Petty Cash Disbursements									
Purchase of £300 Metropolitan 3½ per cent. Stock	1,420	8	10						
Balance in Bank	1	16	7						
" in hands of Treasurer									
Audited and found cor- rect.									
LEONARD TEMPLE THORNE,									
DAVID HOWARD,									
ALFRED JOHN GREENAWAY.									

APPENDIX.

NOMENCLATURE AND NOTATION.

The following instructions relating to these matters were addressed by the Council to the Abstractors in 1879,* and are now reprinted, with a few slight alterations, in the hope that they may have some influence in promoting uniformity of Nomenclature and Notation, especially in Papers communicated to this Journal.

By Order of the Publication Committee,

H. WATTS, *Editor*.

NOMENCLATURE.

"1. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicles, *e.g.*, mercurous and mercuric chloride, sulphurous and sulphuric acid.

"2. Term compounds of metallic and alcoholic radicles with (OH), *hydroxides* and not hydrates, *e.g.*, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation. Compounds such as CH_3ONa , $\text{C}_2\text{H}_5\text{ONa}$, $\text{C}_7\text{H}_{15}\text{ONa}$, &c., should be termed sodium methoxide, ethoxide, heptyoxide, &c.

"3. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3 , H_2SO_4 , H_3PO_4 , and denote the oxides which form acids by names such as sulphuric anhydride or sulphur trioxide. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen-sodium sulphate, hydrogen-disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulae*.

"4. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the $\text{C}_n\text{H}_{2n+2}$ series of the form $\text{CH}_3(\text{CH}_2)_x\text{CH}_3$. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane: for example, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 = \text{propylmethane}$; $\text{CH}_3\text{CH}(\text{CH}_3)_2 = \text{isopropylmethane}$ or *trimethylmethane*; or, although less frequently, by names such as *diisopropyl*.

* See Appendix to Report of Anniversary Meeting, 1879, vol. 35, p. 276.

" 5. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1}.HC:CH.C_nH_{2n+2}$ as α -, and those of the form $CH_2:C(C_nH_{2n+1})_2$ as β -compounds: thus, $CH_3.CH:CH.CH_3 = \alpha$ -dimethylethylene; $CH_2:C(CH_3)_2 = \beta$ -dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH:C.C_nH_{2n+1}$ and $C_nH_{2n+1}.C:C.C_nH_{2n+1}$. Adopt the name *allene* for the hydrocarbon $CH_2:C:CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

" 6. Distinguish all alcohols, *i.e.*, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*, *e.g.*, quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol; furfuraldehyde instead of furfural; fucusaldehyde instead of fucsol. Ethers derived from phenols, such as $C_6H_5.OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oil*, as anisoil and anethoil.

" Alcohols should be spoken of as mono-, di-, tri-, or *n-hydric*, according to the number of OH groups.

" 7. Bodies such as the acids of the lactic series containing the group (OH) should be termed *hydroxy*-, and not oxy-derivatives, *e.g.*, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O , C_6H_5O , $CH_3.COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus ethoxypropionic acid instead of ethylactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetylactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, *viz.*, $C_6H(C_2H_5)_2(OH)_2.COOH$, and not $C_6H_3(OC_2H_5)_2.COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2.COOH$.

" 8. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

" 9. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic acids*, or, failing this, *sulpho-compounds*: as benzene-

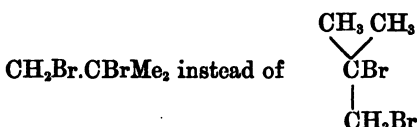
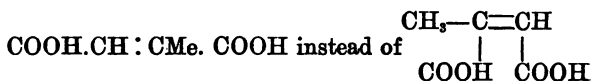
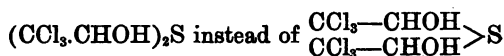
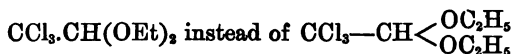
sulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle SO_2NH_2 should be termed sulphonamides.

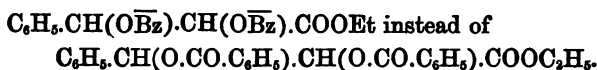
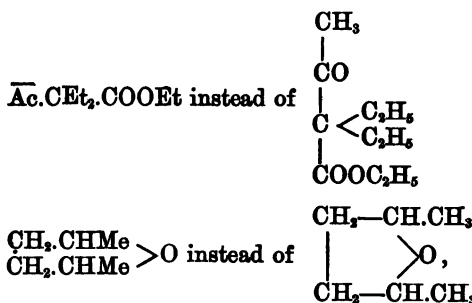
"10. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, e.g., palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide, should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

NOTATION.

"11. Equations, as a rule, should *not* be written on a separate line, but should 'run on' with the text. Simple reactions involving a mere interchange of radicles, or the withdrawal or addition of a particular element or group of elements, need not generally be expressed by equations.

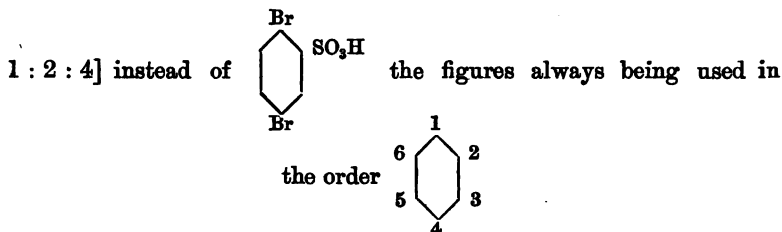
"12. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3 , Et for C_2H_5 , Pr^a for $\text{CH}_3\text{CH}_2\text{CH}_3$, Pr^s for $\text{CH}(\text{CH}_3)_2$, Ph for C_6H_5 , Ac for $\text{CO}\cdot\text{CH}_3$, and Bz for $\text{CO}\cdot\text{C}_6\text{H}_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:—





"13. In representing the constitution of benzene derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, as in the following example:

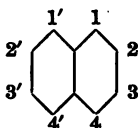
Paradibromobenzenesulphonic acid, $\text{C}_6\text{H}_3\text{Br}_2.\text{SO}_3\text{H}$ [$\text{Br} : \text{SO}_3\text{H} : \text{Br} =$



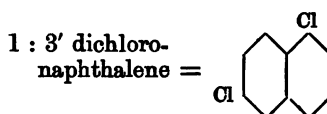
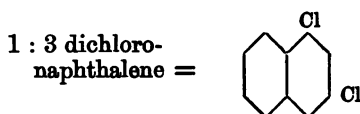
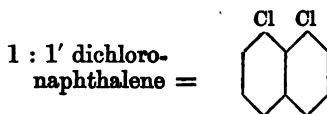
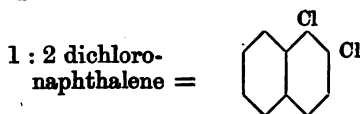
Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them *ortho*- or *meta*-dibromobenzene, &c.

"14. In representing the constitution of derivatives of other 'closed chain' hydrocarbons also, as a rule, do not employ graphic formulæ, but merely indicate the position of the radicles introduced, in the following manner:—

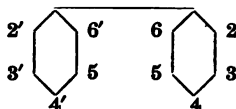
"*In the case of naphthalene*, express the position of the radicles introduced in place of hydrogen relatively to the carbon atoms common to the two 'rings,' and number the positions in the one ring 1, 2, 3, 4, and those in the other 1', 2', 3', 4' in the order shown by the annexed symbol:



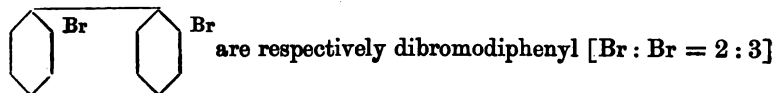
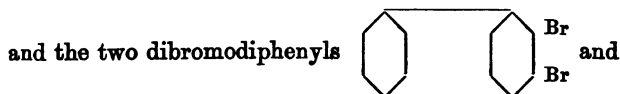
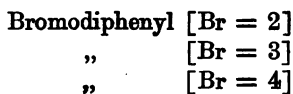
"The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene [Cl : Cl = 1 : 2, &c., thus :—



"In the case of *diphenyl*, indicate the position of the radicles relatively to the carbon atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2', 3', 4', 5', 6', as shown by the following symbol :

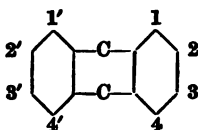


Thus the mono-derivatives, the bromodiphenyls, for example, are represented as



and dibromodiphenyl [Br : Br = 2 : 6'].

"In the case of *anthracene*, employ the following symbol, and indicate the position of the radicles relatively to the central C_2 -group :



Examples :

Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].

Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].

Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3'].

Purpurin, $C_6H_4 : C_2O_2 : C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

" In speaking of compounds such as these, their constitution may be represented by the names

1 : 2 Dihydroxyanthraquinone	= Alizarin.
1 : 4 "	= Quinizarin.
2 : 3' "	= Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquinone	= Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed chain hydrocarbons in square brackets.

PERIODICALS FROM WHICH ABSTRACTS OF PAPERS ARE MADE FOR THE
JOURNAL OF THE CHEMICAL SOCIETY.

General Chemistry and Physics.

Proceedings of the Royal Society of London.

Proceedings of the Royal Society of Edinburgh.

Proceedings of the Royal Society of Dublin.

Proceedings of the Irish Academy.

Scientific Proceedings of the Royal Irish Academy.

Philosophical Magazine.

Chemical News.

American Journal of Science (Silliman's).

American Chemical Journal (Remsen's).

Berichte der deutschen chemischen Gesellschaft.

Annalen der Chemie.

Annalen der Physik und Chemie (Wiedemann's).

Monatshefte für Chemie.

Journal für praktische Chemie.

Chemisches Centralblatt.

Comptes rendus de l'Académie des Sciences.

Annales de Chimie et de Physique.

Bulletin de la Société Chimique de Paris.
Bulletin de l'Académie des Sciences de Belgique.
Gazzetta chimica italiana.
Journal of the Russian Chemical Society.

Mineralogy.

Jahrbuch für Mineralogie (Benecke, Klein u. Rosenbusch).
Zeitschrift für Krystallographie und Mineralogie (Groth).

Animal Physiology.

Pfüger's Archiv für Physiologie.
Zeitschrift für physiologische Chemie.
Zeitschrift für Biologie.

Agricultural Chemistry.

Journal of the Royal Agricultural Society.
Landwirthschaftliche Versuchs-Stationen.
Biedermann's Centralblatt für Agricultur-Chemie.
Annales agronomiques.

Analytical Chemistry.

Fresenius' Zeitschrift für analytische Chemie.
The Analyst.

Technical Chemistry.

Journal of Society of Chemical Industry.
Dingler's polytechnisches Journal.
Bulletin de la Société Industrielle de Mulhouse.
Rübenzuckerindustrie Zeitung.

Pharmacy.

Pharmaceutical Journal and Transactions.
American Journal of Pharmacy.
Archiv der Pharmacie.
Journal de Pharmacie.

XXXV.—*On the Solubility of Glass in Certain Reagents.*

By RICHARD COWPER, A.R.S.M., Demonstrator of Chemistry at the Royal Naval College.

IN the course of certain analytical determinations, I was led to suspect that ammonium sulphide has a considerable solvent action on glass. As this is a point of great importance in analytical work, I have made the following experiments with a view to clear up the matter. 100 c.c. of pure ammonia of sp. gr. 0·88 was evaporated to dryness, and the residue ignited and weighed. It amounted to 0·0015 gram. Ammonium sulphide was made from this ammonia in the usual manner.

Experiments were then conducted in the following way:—

A measured quantity of the reagent was sealed in a tube of hard Bohemian glass, and kept at 100° C. for six days.

It was then neutralised with hydrochloric acid, evaporated to dryness in a platinum dish, and the residue ignited and weighed.

Experiments were made with various reagents besides ammonium sulphide.

The results are shown in the following table.

For purposes of comparison they are calculated on 100 c.c. of the reagent employed.

The actual quantities employed were in Series A 60 c.c., in Series B 40 c.c.

Reagents.		Mgms. dissolved by 100 c.c.	
		A.	B.
H ₂ O	8·0	10·0
H ₂ S	12·5	8·7
Am ₂ S dilute	Prepared from AmHO of sp. gr. 0·982.	49·6	52·5
Am ₂ S concentrated ..	Prepared from AmHO of sp. gr. 0·88.	34·0	47·2
AmHO dilute.....	Sp. gr. 0·982	25·8	42·5
AmHO concentrated..	Sp. gr. 0·88	7·5	7·7
AmHS	Prepared from AmHO of sp. gr. 0·982.	—	51·2

These results show that whilst AmHO of sp. gr. 0·88 scarcely attacks glass (the action not being greater than that exerted by water), dilute AmHO, sp. gr. 0·982, attacks it very considerably. The concentrated Am₂S attacks the glass to very nearly the same extent as

the dilute AmHO, and the dilute Am₂S has more effect than the concentrated reagent.

The following experiment was then made:—

60 c.c. of the dilute Am₂S was evaporated by boiling in a flask until all the sulphur was given off or deposited. It was then transferred to a porcelain crucible, evaporated to dryness, and ignited. The residue amounted to 0.008 gram.

60 c.c. of the same Am₂S, when neutralised with HCl, and then evaporated to dryness, left only 0.001 gram.

This experiment shows that it is not admissible in analytical work to boil a solution of Am₂S in a glass vessel even for a few minutes.

An analysis of some of the residue obtained in the above experiments was then made:—

0.027 gram gave	0.0185 gram	SiO ₂	68 per cent.
	0.0024	„ CaO.....	9 „
	0.0011	„ Al ₂ O ₃	4 „
	0.0052	„ NaCl, KCl	19 „
			100 „

A series of experiments was then made to determine at what degree of dilution the maximum effect on glass was produced by AmHO solutions.

40 c.c. taken.	Mgrams. dissolved.	Calculated in 100 c.c.
AmHO 0.88 1 vol.	9.0	22.5
H ₂ O 1 vol.		
AmHO 0.88 1 vol.	10.5	26.2
H ₂ O 2 vols.		
AmHO 0.88 1 vol.	12.0	30.0
H ₂ O 3 vols.		
AmHO 0.88 1 vol.	10.7	26.7
H ₂ O 4 vols.		
AmHO 1 vol.	16.5	41.2
H ₂ O 5 vols.		
AmHO 1 vol.	12.8	32.0
H ₂ O 6 vols.		

From these experiments it appears that a dilute AmHO, prepared by adding 5 vols. of H₂O to 1 vol. of AmHO of sp. gr. 0.88 (producing a solution having the sp. gr. 0.982), has the maximum effect.

XXXVI.—*Analysis of a Piece of Oxidised Iron from the Condenser of H.M.S. "Spartan."**

By RICHARD COWPER, A.R.S.M., Demonstrator of Chemistry at the Royal Naval College.

THE specimen formed part of the tank of a surface condenser. It would thus, whilst the condenser was in use, be constantly subjected to the action of warm sea-water at a temperature not exceeding about 100° F.

It consisted of a brownish substance in which were imbedded numerous shining black particles, and resembled very much in appearance a piece of rusty grey pig-iron. It was, however, very light, having a sp. gr. of 2.63 only, and extremely friable. When heated the substance gave off water and strongly acid fumes, which were found to consist of hydrochloric acid. When it was treated with hydrochloric acid, no hydrogen was evolved, and on digestion with cupric chloride no copper was precipitated. All the iron is therefore oxidised.

4 grams of the substance, after treatment with hydrochloric acid and evaporation to dryness, gave 1.2987 grams = 32.47 per cent. of insoluble residue. The solution was treated with H_2S .

The precipitate produced was shown to contain no Pb, As, Sn, or Sb. 0.015 gram = 0.375 per cent. of CuO was obtained. A fourth part of the HCl solution was then taken, and iron, alumina, and phosphoric acid, separated by sodium acetate. From this precipitate the alumina was separated by the $Na_2S_2O_3$ process. The precipitate so obtained weighed 0.0037 gram, and was calculated as aluminium phosphate. Iron was precipitated by Am_2S , and converted into Fe_2O_3 . 0.4919 gram Fe_2O_3 = 34.43 per cent. Fe was obtained. In the filtrate from the FeS , phosphoric acid was determined as $Mg_2P_2O_7$. 0.0785 gram = 0.0502 P_2O_5 was obtained.

Adding to this the small quantity of P_2O_5 in the 0.0037 gram of aluminium phosphate, we have total P_2O_5 = 0.0523 gram = 5.23 per cent. P_2O_5 was also determined by precipitating, first as ammonium phosphomolybdate, and subsequently obtaining it as $Mg_2P_2O_7$. From 1 gram 0.083 gram $Mg_2P_2O_7$ = 5.31 per cent. P_2O_5 was obtained.

In the filtrate from the sodic acetate precipitate Mn was determined by precipitation with Na_2CO_3 .

* Dr. Percy was good enough to send me a piece of iron from the condenser of H.M.S. "Spartan." In order to ascertain the result of the action of warm sea-water on cast iron, I requested Mr. Cowper to make an analysis of the substance.

(Signed) H. DEBUS.

0.013 gram $\text{Mn}_3\text{O}_4 = 0.0107$ gram Mn_2O_3 was obtained. In a separate experiment, 1 gram of the substance gave 0.005 gram = 0.05 per cent. of cobalt oxide. Subtracting this from the Mn_2O_3 , we have $1.07 - 0.05 = 1.02$ per cent. Mn_2O_3 .

In order to ascertain the amount of ferrous oxide present, some of the substance was dissolved in HCl in an atmosphere of CO_2 , and allowed to subside. A portion of the clear liquid was titrated with standard $\text{K}_2\text{Cr}_2\text{O}_7$. 0.9619 gram required 31.64 c.c. normal $\text{K}_2\text{Cr}_2\text{O}_7 = 0.3164$ gram Fe = 34.89 c.c. Fe = 42.29 per cent. FeO.

The total Fe being 34.43 per cent., there is 1.54 per cent. of Fe present as $\text{Fe}_2\text{O}_3 = 2.20$ per cent. Fe_2O_3 .

0.637 gram of the substance was boiled with HCl and a piece of metallic copper, the air being excluded as much as possible. 0.9565 gram of Cu lost 0.0112 gram = 0.0143 gram $\text{Fe}_2\text{O}_3 = 2.22$ per cent.

Some of the residue, insoluble in HCl, was warmed with NaHO solution. The NaHO scarcely became coloured, showing the presence of only a small quantity of combined carbon. Another portion of this insoluble residue, which had been dried at 100°C ., was further dried at 120° , losing 1.94 per cent.

It was then burnt with a mixture of lead chromate and potassium bichromate, the following numbers being obtained:—

0.2386 gram gave 0.0161 gram $\text{H}_2\text{O} = 0.75$ per cent. H.

0.3459 gram $\text{CO}_2 = 0.0943 \text{ C} = 39.53$ per cent.

Calculated on the original substance—

$\text{H}_2\text{O} = 2.15$ per cent. = 0.24 per cent. H. C = 12.57 per cent.

0.4791 gram of the original substance was burnt with the mixed lead and potassium chromates, and gave—

0.0904 $\text{H}_2\text{O} = 18.86$ per cent.

0.2156 $\text{CO}_2 = 0.0588 \text{ C} = 12.27$ per cent.

From this 18.86 per cent. H_2O was subtracted, the 2.15 per cent. found on burning the residue dried at 120°C ., leaving 16.71 per cent. of H_2O .

0.5 gram of insoluble residue, on being burnt in a platinum crucible, left 0.2702 gram of residue = 54.04 per cent. = 55.08 on the residue dried at 120°C ., or 17.53 per cent. on the original substance.

Of the incombustible portion 0.3563 gram was fused with K_2CO_3 and Na_2CO_3 , and treated for SiO_2 , &c., in the usual manner.

The following numbers were obtained:—

0.3449 gram SiO_2	=	16.98	per cent. on original substance.
0.0024 „ Fe_2O_3	=	0.12	„ „ „
0.0012 „ Al_2O_3	=	0.06	„ „ „
0.0056 $\text{CaCO}_3 = 0.0031 \text{ CaO}$	=	0.15	„ „ „
0.0012 $\text{Mg}_2\text{P}_2\text{O}_7 = 0.0004 \text{ MgO}$	=	0.02	„ „ „

To determine sodium salts, 1.534 gram of the substance was extracted with water, a few drops of AmHO added, evaporated to dryness with HgO and ignited, and the residue treated with H₂O. The solution was filtered and evaporated to dryness in a platinum crucible. 0.0039 gram was obtained. It consisted chiefly of sodium sulphate.

0.0039 gram Na₂SO₄ = 0.0017 gram = 0.11 per cent. Na₂O.

Chlorine was determined by treating the original substance with dilute nitric acid, and precipitating with AgNO₃. 0.9451 gram gave 0.0794 AgCl = 0.0196 = 2.078 per cent. Cl.

Sulphuric acid was determined by BaCl₂. 1 gram gave 0.009 gram BaSO₄ = 0.0031 gram. = 0.31 per cent. SO₃.

An examination was made for vanadium, by heating some of the substance with KNO₃, extracting with water, and adding AmHO and a piece of AmCl. The solution, after standing, was filtered. The residue was washed with a saturated solution of AmCl and ignited and weighed. 0.0011 gram of substance was thus obtained.

It gave, with borax in the outer flame, a yellow-green bead, in the inner flame a bead which was brown hot, and green cold.

Collecting all these results we have—

Insoluble residue dried at 120° C.. 30.14	{	Carbon 12.57	{	Silica 16.98
		Hydrogen .. 0.24		Ferric oxide 0.12
		Incombustible 17.54*		Alumina .. 0.06
				Lime 0.15
				Magnesia.. 0.02

Cupric oxide	0.38
Ferric oxide	2.21
Ferrous oxide	42.33
Alumina	0.16
Manganic oxide ..	1.02
Cobalt oxide	0.05
Sodium oxide	0.11
Phosphoric acid ..	5.24
Sulphuric acid ..	0.31
Vanadic acid	0.11
Chlorine	2.08
Water	16.71

100.85

* The sum of the several constituents of the incombustible matter is 17.33, whereas the amount found by direct experiment was 17.54. The difference may be ascribed to the presence of some constituent not determined, or to error in experiment.

It will be seen from these results that the iron has been completely oxidised, chiefly, however, only to the protoxide.

This great preponderance of FeO over Fe_2O_3 has been observed by Professor Liversidge in a piece of oxidised iron from the blade of a screw propeller (*Proc. Roy. Soc. of N.S. Wales*). The action in this case must be considered as chiefly due to sea-water, but at ordinary temperatures.

If we take 2.5 as the ordinary percentage of graphite in foundry pig, it is clear that more than 90 per cent. of the iron has been removed, if we suppose that the graphite has entirely remained.

The greater part of the combined carbon has disappeared.

With the probable exception of sulphur, the percentages of all the other constituents of the pig-iron have increased.

Especially remarkable is the large proportion of chlorine which is present in combination with iron and manganese.

An aqueous extract of the original substance contained FeO , equivalent to 1.65 per cent., and $\text{MnO} = 0.49$ per cent. of the substance.

In striking contrast with this rusting of iron in sea-water is the rusting of iron in moist air. A sample of ordinary iron rust, scraped from some cast iron which had been exposed for some time to the atmosphere, gave on analysis 65.42 per cent. of ferric oxide and 7.42 per cent. of ferrous oxide.

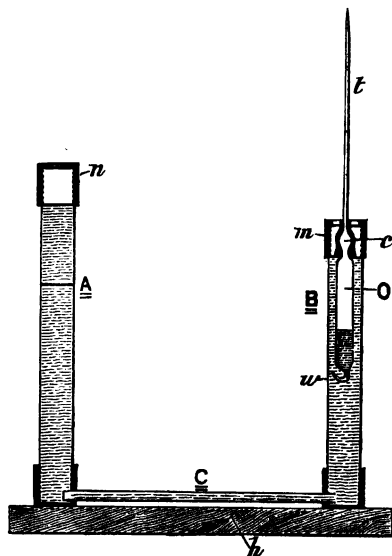
XXXVII.—*Note on a convenient Apparatus for the Liquefaction of Ammonia.*

By J. EMERSON REYNOLDS, M.D., F.R.S., Professor of Chemistry,
University of Dublin.

THE annexed engraving represents a piece of apparatus that I employ with advantage in illustrating the principle of Carré's machine, and in demonstrating the liquefaction of ammonia gas by pressure. It is so easily managed, strong, and inexpensive, that I think it will be found a useful addition to the apparatus of the lecture table, and as such I beg to lay its description before the Society.

A species of U-tube of stout wrought iron is made of the form shown in the figure, A, B, C. A is about 40 cm. long, B 30 cm., and each is 12 cm. in internal diameter; C is about 25 cm. long, and 5 or 6 mm. internal diameter, and is securely screwed into the two wider tubes.

The whole is fastened to the wooden stand *h*. *A* is provided with a stout screw-cap *n*, and the joint is rendered gas-tight by a leather



washer. *B* is also fitted with a strong screw-cap, *m*, provided with a deep head, through which a conical hole is bored; the long glass tube *t* of the apparatus *tO* passes through this hole to the expansion *c*, which should fit into the cone, and be there secured by any good cement. The screw-cap *m* therefore carries the glass apparatus, which latter is a form of pressure-tube now easily obtained through good instrument makers. The liquefaction takes place within the glass tube *t*, which must, of course, be sufficiently strong. The length of this tube is about 25 cm.; the wide reservoir *O* must have at least ten times the capacity of *t*; the reservoir *O* terminates below in a rather narrow curved tube *w*, which is always open.

The glass apparatus is filled in the usual way with dry ammonia gas by connecting *w* with an apparatus affording a current of the pure gas.

When the air has been expelled—and a good current maintained for ten minutes sufficiently effects this—the flow of gas is allowed to slacken, and the capillary end of *t* is securely sealed at the blowpipe. The tube is removed from *w*, and the latter at once dipped in mercury, which enters and so prevents escape of ammonia.

The cap *n* is now removed and mercury is poured into *A* until the

metal rises nearly to the top of B; O is then introduced into B, allowing the mercury displaced to overflow into a vessel placed to receive it, and the cap *m* is screwed home. This cap must, of course, be provided with a good leather washer.

We have, therefore, nothing but mercury between the gas in *o* and the surface of the metal in A. Next remove enough mercury from A by a pipette to leave a space of some 12 cm. between the surface of the metal and the cap; then fill up to the top with the strongest "solution of ammonia," and screw down the cap *n*. The apparatus is then ready for experiment, which is performed in the following way:—

Gradually heat the portion of A containing the solution of ammonia by a Bunsen flame occasionally applied. As the temperature rises, ammonia is expelled from the solution; but since the gas has no escape, considerable pressure is exerted in A on the surface of the mercury, and the latter, acting as a fluid piston, compresses the gas in O, which latter steadily diminishes in volume until at last the mercury rises into view in *t*; and if the heating of A be now carefully managed, a layer of colourless liquid ammonia is seen to form on the surface of the mercury in *t* as the compression proceeds.

If the joints are well made and the heating properly managed, it is easy to maintain a steady pressure for a considerable time, but anything like violent heating must at all times be carefully avoided. On allowing the apparatus to cool, the mercury recedes in *t*, and the liquefied ammonia disappears. This apparatus is always ready for experiment, though it is desirable to unscrew the cap of A occasionally, and change the solution of ammonia, as slow leakage from *w* is inevitable.*

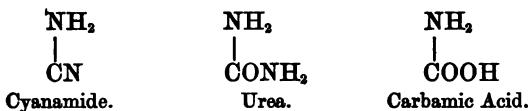
It is obvious that the principle involved is one of general application to the liquefaction of gases, as the mechanical effect depends upon the temperature to which the tube A is raised.

* This apparatus was made for me by Messrs. Yeates and Son, of Dublin.

XXXVIII.—Transformation of Urea into Cyanamide.

By H. J. H. FENTON, M.A., Demonstrator of Chemistry in the University of Cambridge.

It is well known that cyanamide when treated with dilute acids takes up the elements of water, forming urea : $\text{CN}_2\text{H}_2 + \text{OH}_2 = \text{CON}_2\text{H}_4$. In fact, if the ordinary view with regard to the constitution of these bodies be accepted, cyanamide may be considered as the nitril of carbamic acid, of which urea is the amide :—



Ammonium carbamate loses water, forming urea (Basaroff, *Chem. Soc. J.* [2], 6, 194), and thio-urea can be readily caused to part with the elements of hydrogen sulphide, giving cyanamide.

Drechsel has also obtained cyanamide by the action of moist carbon dioxide on ammelide, and the latter, it is stated, is met with among the products of the decomposition of urea by heat. But the direct dehydration of urea into cyanamide has not hitherto been effected (Drechsel, *J. pr. Chem.* [2], 11, 209).

Attempts were made in this direction by acting upon urea with phosphorus pentoxide, calcium chloride, and other ordinary dehydrating agents, but in none of these cases was any cyanamide produced. When, however, urea is gently heated with metallic sodium, a violent reaction takes place, and a large quantity of hydrogen is evolved, which takes fire and burns at the mouth of the vessel. The solid residue which remains dissolves almost completely in water, and the solution so obtained gives abundantly the characteristic reactions of cyanamide; namely, a bulky yellow precipitate with silver nitrate, nearly insoluble in cold ammonia, but readily soluble in dilute nitric acid, and a brownish-black precipitate with cupric salts.

In order to obtain the cyanamide from this solution (which must obviously contain it as the sodium derivative), ammonia in excess and silver nitrate were added, and the yellow precipitate obtained was thoroughly washed and dried, covered with ether, and subjected to the action of hydrogen sulphide.

The ethereal solution was filtered from silver sulphide, and evaporated at a gentle heat. The residue thus obtained had the characteristic property of remaining liquid until touched with a pointed body, when it immediately crystallised. The crystals were carefully dried over strong sulphuric acid, and analysed by a modifi-

cation of Gottlieb's method, i.e., weighed quantities of the substance were burnt in a vacuum with copper oxide, and the resulting carbon dioxide and nitrogen collected and measured in the ordinary way:—

0.0412 gram treated in this manner gave—

			Theory (CN ₂ H ₂).
CO ₂	21.5	c.c. (corr.)	21.95 c.c.
N	21.28	„	21.95 „

0.0346 gram gave—

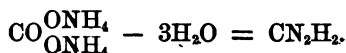
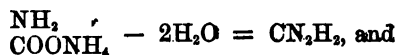
CO ₂	18.15	c.c.	18.43 c.c.
N	18.24	„	18.43 „

The formation of cyanamide in the above reaction may be represented by the equation—



the cyanamide being then further acted upon by sodium, producing the disodium derivative CN₂Na₂.

It was natural from the above results, to expect that ammonium carbamate and ammonium carbonate would behave similarly when acted upon by metallic sodium—



And such was found to be the case, a fairly good yield of cyanamide being obtained in each instance, although it is impossible to prevent considerable loss from volatilisation of the unaltered material, which is not the case to any extent with urea.

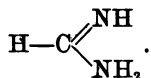
The above reactions afford very convenient methods for the preparation of cyanamide, especially the action of sodium upon urea, by which it is easy to prepare considerable quantities of cyanamide in a comparatively short time.

I am at present engaged in analysis of the yellow silver-derivative of cyanamide. The percentage of silver, in samples prepared under varying conditions, appears to be always intermediate between the values required by theory for CN₂HAg and CN₂Ag₂; whilst the colour varies from a very pale-yellow to a bright canary-yellow, according to the manner in which the substance is prepared.

XXXIX.—On the Action of Haloid Acids upon Hydrocyanic Acid.

By L. CLAISEN, Ph.D., and F. E. MATTHEWS, F.C.S.

GAUTIER (*Liebig's Annalen*, **145**, 118) has already published the action of anhydrous hydrochloric acid upon hydrocyanic acid. He saturates anhydrous hydrocyanic acid with dry hydrochloric acid at a temperature of -10° C., and afterwards heats the mixture, sealed in glass vessels, to $30-40^{\circ}$. On cooling, a colourless crystalline substance separates out, which, on analysis, agrees with the formula $\text{HCN} + \text{HCl}$. On treatment with alcohol, this substance gave formic ether, ethyl chloride, ammonium chloride, and the hydrochloride of a base—



Pinner and Klein (*Berl. Ber.*, **11**, 1475) expected to obtain the salt of the imide ether of formic acid, $\text{H}-\text{C} \begin{array}{l} \diagup \text{NH} \\ \diagdown \text{OC}_2\text{H}_5 \end{array}$, by passing hydro-

chloric acid gas through a mixture of anhydrous hydrocyanic acid and alcohol; instead, however, of obtaining either this ether or Gautier's base, they arrived at the ether and amide of diethylglyoxylic acid, $\text{CH}(\text{OC}_2\text{H}_5)_2.\text{COOC}_2\text{H}_5$.

It seemed probable to us that the diethylglyoxylic acid was formed in the following manner: the hydrochloric acid first acts upon the hydrocyanic acid in presence of alcohol and produces formic ether. This formic ether then unites with some undecomposed hydrocyanic

acid to form a nitril, $\begin{array}{c} \text{CH} < \text{OC}_2\text{H}_5 \\ \text{OH} \\ | \\ \text{CN} \end{array}$, which, by the further action of hydrochloric acid and alcohol, gives diethylglyoxylic ether.

To test the truth of the hypothesis, we mixed together formic ether and hydrocyanic acid; but after allowing them to stand together for several weeks, no evidence of a reaction was to be observed; however, on passing hydrochloric acid gas through the mixture, a reaction at once took place, and a white crystalline substance separated out. We further found that this substance was an addition-product of hydrochloric and hydrocyanic acids, and that the substance was not the compound $\text{HCN}.\text{HCl}$ obtained by Gautier. We therefore thought it would be of interest to study the constitution and some of the reactions of this remarkable substance. After some preliminary experiments we found that other ethers, such as acetic and benzoic ethers,

acted equally well, and that the ether itself played no part in the reaction. For the preparation of the substance, ordinary acetic ether was distilled several times over phosphoric anhydride, so as to thoroughly dry it and free it from alcohol. The prussic acid was prepared according to Wöhler's (*Liebig's Annalen*, 73, 219) directions, and was thoroughly dried over calcium chloride, and when so obtained it did not show the slightest trace of decomposition in three weeks. The pure acetic ether was then added to about an equal bulk of the hydrocyanic acid in a strong glass cylinder. The cylinder was now immersed in a mixture of ice and salt, and a stream of hydrochloric acid passed into it. The gas was abundantly absorbed, and after some time small crystals separated out, and in three or four hours the contents of the cylinder became nearly solid. The stream of gas was then discontinued and the substance washed with more acetic ether, powdered under the surface of this liquid, and then washed several times more with absolutely dry ether, after which it was subjected to a current of dry air.

It gave the following results on analysis:—

Gram.			Gram.		Gram.				
{ 1. 0.3550 substance gave			0.1984 CO ₂ ; and		0.1128 H ₂ O.				
{ 2. 0.2444 "			0.1296 "		0.0753 "				
{ 3. 0.4230 "			0.2330 "		0.1263 "				
{ 4. 0.1925 "			0.4807 AgCl, and		0.02 Ag.				
{ 5. 0.1832 "			0.4828 AgCl.						
{ 6. 0.4134 "			0.4860 Pt.						
{ 7. 0.2630 "			0.3125 "						

	Theory for		Found.						
	2HCN + 3HCl.		1.	2.	3.	4.	5.	6.	7.
C ₂ ..	24.0	14.68	15.23	14.46	15.02	—	—	—	—
H ₆ .	5.0	3.06	3.52	3.42	3.22	—	—	—	—
N ₄ .	28.0	17.12	—	—	—	—	—	16.68	16.86
Cl ₃ .	106.5	65.14	—	—	—	65.14	65.19	—	—
	163.5	100.0							

These results agree with the formula 2HCN + 3HCl, but are entirely discordant with the formula HCN + HCl. The above analyses were performed on various portions made at different times, and in no one case did the result point to the formula HCN + HCl.

The substance, 2HCN + 3HCl, is a colourless crystalline mass, inodorous in dry, and fuming strongly in moist air. It appears to be only slightly poisonous, and on solution in water shows only traces of prussic acid, probably present as an impurity in the original com-

pound. It is insoluble in ethylic, formic, or acetic ethers, soluble, but with decomposition, in water and alcohol. On exposure to air, it is rapidly converted into ammoniac chloride and formic acid.

To study its decomposition with alcohol, about 100 grams were dissolved in the liquid, and the mixture was afterwards heated on the water-bath for about three hours. Hydrochloric acid and ethyl chloride were evolved, and ammonium chloride separated out in large quantities. The liquid was filtered off from the sal-ammoniac and distilled. It began to boil at 30° , and between this temperature and 60° a fair amount distilled over. This distillate proved afterwards to be formic ether, and after thorough purification boiled at $54-57^{\circ}$.

The alcohol was next distilled off, and the residual liquid soon solidified on cooling. It was insoluble in ether, but exceedingly soluble in alcohol and in water. To free it from the last traces of ammonium chloride, it was crystallised several times from alcohol.

A chlorine determination was made—

0.29 gram substance gave 0.509 gram AgCl.

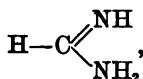
Theory for $\text{CH} \begin{smallmatrix} \text{NH} \\ \text{NH}_2, \text{HCl} \end{smallmatrix}$	Cl. . . .	44.09 per cent.
	found Cl. . . .	43.42 „

The platinochloride was made in the usual way and the Pt determined.

0.1425 gram substance gave 0.056 gram Pt.

$\left(\text{CH} \begin{smallmatrix} \text{NH}_2 \\ \text{NH.HCl} \end{smallmatrix} \right)_2 \text{PtCl}_4$	Platinum: theory..	39.40
	found..	39.29

The solid therefore obtained by the action of the substance, $2\text{HCN} + 3\text{HCl}$, upon alcohol is the hydrochloride of the base—



or *formamidine*. It is colourless, and crystallises from alcohol partly in warty masses and partly in flat transparent plates, which can be prepared nearly two inches long. It melts at 81° , and in fact perfectly agrees with Gautier's description.

Having studied the action of hydrochloric acid upon hydrocyanic in the presence of acetic ether, we thought the corresponding experiment with hydrobromic acid would be of interest.

The hydrobromic acid was prepared by decomposing phosphorous

bromide with water and drying the product with phosphoric anhydride. The rest of the experiment was conducted in precisely the same manner as has been described in the case of hydrochloric acid. A colourless, very hygroscopic substance was obtained, which gave the following results on analysis:—

1. 0.1623 gram substance gave 0.3048 gram AgBr.	
2. 0.4286 " "	0.8049 " AgBr.
3. 0.1414 " "	0.2651 " AgBr.
4. 0.1700 " "	0.0975 " Pt.
5. 0.1357 " "	0.0777 " Pt.

Theory for 2HCN, 3HBr.		Found.				
		1.	2.	3.	4.	5.
Br.....	80.8	79.91	79.9	79.78	—	—
H.....						
C.....						
N.....	9.42	—	—	—	8.01	8.13

From these analyses it will be seen that both the bromine and the nitrogen come out considerably too low, probably on account of the extremely hygroscopic nature of the body. It is a colourless substance, soluble with violent decomposition in water and alcohol. A body of the above formula has already been obtained by Gal by the direct union of hydrobromic and hydrocyanic acids. We also attempted to prepare formamide by the direct addition of water to prussic acid. A weighed amount of prussic acid was put into a small flask and the theoretical amount of the strongest fuming hydrochloric acid added to it. The mixture was well cooled, and when the reaction appeared to be over, the mixture was put into an exhausted desiccator over soda-lime, and allowed to stand some weeks. It was afterwards fractionated. The chief portion boiled at 195—220°, and came over as a thick liquid. A nitrogen determination was made, but the result came out 2 to 3 per cent. below the theoretic; this must have been due to the impurity of the formamide, probably through intermixture with some formic acid, as no other compound which could have been formed in the reaction could boil anywhere near 200° C.

In conclusion, we wish to point out that when hydrocyanic acid unites with haloïd acids in presence of ethers, a simple addition-compound is not formed, but a more complex one, 2 mols. of the prussic acid uniting with the haloïd acid; and it seems doubtful to us whether Gautier's compound HCN, HCl is not identical with the compound whose formula we have found to be 2HCN + 3HCl. The two substances resemble one another physically, and give absolutely the same reactions with water and with alcohol. Gautier's method of

preparation is difficult, not to say dangerous, and the purification of a body so hygroscopic as this must be attended with an immense amount of difficulty. It is particularly satisfactory to us to have rediscovered and found a comparatively easy method of preparing a body of such great interest as formamidine, especially as the researches of Pinner and Klein threw great doubts on its existence.

XL.—*On the Action of Acetyl Chloride on Fumaric Acid.*

By W. H. PERKIN, F.R.S.

LAST autumn I gave an account of some experiments on this subject (*Chem. Soc. J.*, 1881, 560; *Ber.*, 14, 2546), and stated that, although pure acetyl chloride was without action on fumaric acid at the temperature of 100° C., yet, on the addition of acetic acid to the mixture, it was attacked and gradually dissolved, with formation of maleic anhydride. In the same paper I also showed that by the action of acetyl chloride on malic acid, aceto-malic anhydride was formed, and that this body when distilled underwent decomposition, yielding maleic anhydride and acetic acid. Anschütz (*Ber.*, 14, 2792), who obtained results similar to mine, endeavoured to explain the influence of acetic acid on a mixture of acetyl chloride and fumaric acid, by assuming that it combined with the fumaric acid, forming aceto-malic acid, which was then converted into aceto-malic anhydride by the acetyl chloride, and that this anhydride on distillation yielded maleic anhydride and acetic acid.

In my paper, however, I did not say that the formation of maleic anhydride in this reaction was considered proved by the fact of its being obtained by distilling the product of the reaction, and I certainly should not have been satisfied by such a method alone. The process I used consisted in diluting the product from the sealed tube with water, which would convert any maleic anhydride if present into maleic acid, and evaporating the solution over the water-bath with hydrochloric acid. In this way maleic acid is rapidly converted into fumaric acid, which, on account of its slight solubility, is easily recognised. On employing this method, fumaric acid was obtained in abundance. The distillation process also gave maleic anhydride.

As Anschütz's remarks on this reaction were calculated to throw doubt upon some of my conclusions, I was induced to make fresh experiments on the subject; and first of all, to prove the incorrectness of the theory above given, a solution of aceto-malic acid was

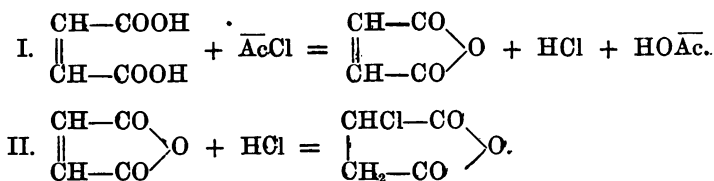
evaporated with hydrochloric acid, to see if it would yield fumaric acid; as was expected, however, it did not produce any.

Anschütz and C. Bennert (*Ber.*, 15, 640) have just published some fresh observations on the action of acetyl chloride and acetic acid on fumaric acid, and have given a fresh explanation of the reaction. The results they have described agree in most respects with those I have obtained. They show that in this reaction chlorosuccinic anhydride is produced, as well as maleic anhydride, and explain the reaction by assuming that the acetyl chloride acting on the acetic acid yields hydrochloric acid and acetic anhydride, the hydrochloric acid thus produced giving with fumaric acid, chlorosuccinic acid, which is then converted into chlorosuccinic anhydride by the acetyl chloride. This theory, however, does not account for the formation of maleic anhydride, as they admit; it also assumes that chlorosuccinic anhydride should be the chief product.

In the experiments I have made on the subject and repeated several times, both in the way I originally made them, and also by distilling under reduced pressure (10 mm. of mercury), I have invariably found that maleic anhydride is the chief product of the reaction, being formed in considerably larger quantities than chlorosuccinic anhydride.

Contrary to the observations of Anschütz (*Ber.*, 14, 2792) I find that acetyl chloride alone (b. p. 55—56°), when heated in a sealed tube with fumaric acid to 140° for seven or eight hours, acts upon it, forming a clear fluid, the sides of the tube being only very slightly stained with a brown product. On distilling under reduced pressure, maleic anhydride was obtained as the chief product, the rest being chlorosuccinic anhydride.

From these observations it appears to me that acetyl chloride acts upon fumaric acid in the same way as it does on other dibasic acids, forming the anhydride by the removal of a molecule of water, the anhydride in this case being maleic anhydride; and as a secondary result, part of the maleic anhydride thus formed unites with the hydrochloric acid present, and forms chlorosuccinic anhydride, thus—



In this way the production of both products is simply explained, and from direct experiment I have proved that maleic anhydride,

when heated in a sealed tube to 100° with acetic acid saturated with hydrochloric acid, yields chlorosuccinic anhydride.

The fact that fumaric acid can be combined with hydrochloric acid to form chlorosuccinic acid, and that this, when heated with acetyl chloride, gives chlorosuccinic anhydride, as shown by Anschütz and Bennert, does not prove much, if anything, in regard to this reaction, and as already stated it does not account for the formation of the principal product, maleic anhydride.

It is believed that the reason why the reaction between acetyl chloride and fumaric acid takes place at a lower temperature when acetic acid is present, is due to its being a solvent for fumaric acid.

XLI.—*On the Action of Acetone on Phenanthraquinone, both Alone and in Presence of Ammonia.*

By FRANCIS R. JAPP, M.A., Ph.D., Assistant Professor of Chemistry in the Normal School of Science, South Kensington; and FREDK. W. STREATFEILD.

THE results obtained by acting with aldehydes upon phenanthraquinone in presence of ammonia (this Journal, 1880, 666; 1881, 225; 1882, 149), led us to examine whether any action occurs when ketones are substituted for aldehydes. Since in the reaction with aldehydes the hydrogen-atom of the COH-group is eliminated, it was evident that any reaction with ketones must possess an essentially different character.

After satisfying ourselves that phenanthraquinone, acetone, and ammonia react very readily at ordinary temperatures, we adopted the following mode of conducting the experiment:—

50 grams of finely-powdered phenanthraquinone were mixed in a thick-walled flask with 60 grams of acetone. (The acetone employed had been purified by conversion into the double compound with hydrogen sodium sulphite; but we have since found that a rectified acetone, boiling between 56° and 58° , answers the purpose equally well.) About 40 c.c. of strong aqueous ammonia were then added, the flask was tightly corked, and the contents were thoroughly mixed by shaking. After standing for a few minutes, the mixture became perceptibly darker in colour, and this change was accompanied by a rise in temperature. A slight pressure was relieved by removing the cork from time to time. The temperature continued to rise, the contents of the flask again became lighter in colour, and the quinone appeared to be

converted into a white granular crystalline powder, whilst the supernatant liquid remained dark-coloured. The reaction was now complete. It is worthy of note that no two of the three substances taking part in this reaction—phenanthraquinone, acetone, and aqueous ammonia—react in the cold without the third. As soon as the temperature had sufficiently fallen, ether was added, and the crystalline substance was filtered off and washed with ether. In this way the substance was obtained almost colourless, but examination with a lens showed the presence of small particles of unaltered quinone.

In attempting to purify the substance by recrystallisation, it was found that it readily underwent decomposition. It dissolved in hot alcohol; but the solution smelt of ammonia, became dark-coloured, and on cooling deposited a brown substance which had the appearance of impure phenanthraquinone. An alcoholic solution, saturated in the cold, yielded by spontaneous evaporation colourless rhomboïdal plates, but these were mixed with a quantity of gummy matter. At last, by taking advantage of the fact that the decomposition of a substance occurs less readily in presence of an excess of its products of decomposition, we succeeded in obtaining the new compound in a state of purity. The crude product was dissolved in boiling acetone (b. p. 56–58°), to which a small quantity of aqueous ammonia had been added. The filtered solution deposited on cooling a small quantity of the new substance in colourless rhomboïdal laminæ. By spontaneous evaporation over sulphuric acid, the quantity of crystalline substance increased. The crystals were filtered off, washed with ether, and dried over sulphuric acid. Care must be taken not to leave them too long in contact with the acetone solution, otherwise they redissolve, and only a gummy mass is obtained by further evaporation. The yield of pure substance is small. The fusing point could not be determined with accuracy, since when heated in a capillary tube, the compound begins to change colour about 120°, gradually becoming darker, till at about 130° it fuses, turning black and evolving gas.

Analysis yielded the following results:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1004	0.2824	0.0538
II.	0.1185	0.3341	0.0624

III. 0.1047 gram burnt with copper oxide in a vacuum gave 4.75 c.c. moist nitrogen at 16.5° and 757 mm. pressure, corresponding to 0.0055 gram nitrogen.

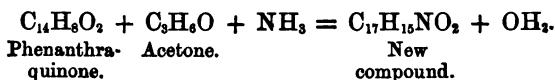
IV. 0.1283 gram gave 5.80 c.c. moist nitrogen at 16.5° and 766 mm. pressure, corresponding to 0.0068 gram nitrogen.

These numbers lead to the formula C₁₇H₁₃NO₂.

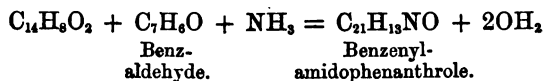
	Calculated for $C_{17}H_{15}NO_2$.		Found.				Mean.
			I.	II.	III.	IV.	
C_{17}	204.	76.98	76.71	76.89	—	—	76.80
H_{15}	15	5.66	5.94	5.85	—	—	5.89
N	14	5.28	—	—	5.25	5.30	5.27
O_2	32	12.08	—	—	—	—	(12.04)
	265	100.00	—	—	—	—	100.00

Another preparation of the substance was analysed with the same result.

The formation of a compound of the above formula would be expressed by the equation—



For the sake of comparison the equation for the reaction with a non-hydroxylated aldehyde may also be given:—



(this Journal, 1880, 669).

The relative molecular quantities of the three generating substances are thus the same in both reactions, but in the case of the aldehyde twice as much water is formed as in the case of the ketone. This is explained by the fact, already alluded to, that in the aldehyde reaction the hydrogen-atom of the COH-group is eliminated.

As we suspected that the compound $C_{17}H_{15}NO_2$ contained an NH-group, we examined the action of acetic anhydride upon it, but found that this reagent decomposed it, even in the cold, with regeneration of phenanthraquinone.

Behaviour of the Compound $C_{17}H_{15}NO_2$ towards Acids.—The substance dissolved readily in cold concentrated hydrochloric acid, yielding a pale yellow solution, which speedily became green and turbid. After standing for about a day, the solution deposited a dark indigo-blue substance, the nature of which we have not yet been able to ascertain, as it appears to undergo decomposition when treated with solvents. The filtrate from this blue substance became turbid on adding a small quantity of water, but the addition of a larger quantity caused it to become clear again. On standing, this clear dilute solution again became turbid, and gradually deposited a substance in fine colourless needles. These were dissolved in ether, and the solution allowed to evaporate. The substance was thus obtained in large, thin, colourless

blades, with parallel edges. After two or three crystallisations it fused constantly at $89.5-90^\circ$. Qualitative tests showed that it contained neither nitrogen nor chlorine.

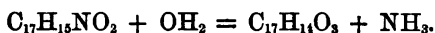
Analysis yielded the following results:—

	Substance.	CO ₂ .	OH ₂ .
I.....	0.1677	0.4683	0.0802
II.....	0.1490	0.4178	0.0712

These numbers lead to the formula $C_{17}H_{14}O_3$.

	Calculated for $C_{17}H_{14}O_3$.		Found.		
			I.	II.	Mean.
C ₁₇	204	76.70	76.47	76.66	76.56
H ₁₄	14	5.26	5.30	5.34	5.32
O ₃	48	18.04	—	—	18.12
	266	100.00	—	—	100.00

In the formation of this compound from the compound $C_{17}H_{15}NO_2$, the elements of water have been added, and the elements of ammonia eliminated:—

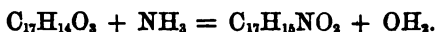


In confirmation of this view we found that the hydrochloric acid filtrate from the needle-shaped crystals yielded ammoniac chloride on evaporation. The formation of the insoluble blue compound must therefore be regarded as the result of a totally distinct reaction. In fact we found that by substituting other acids for hydrochloric, the formation of the blue compound was avoided. Thus by dissolving the compound $C_{17}H_{15}NO_2$ in concentrated aqueous oxalic acid, and afterwards diluting, a large yield of the compound $C_{17}H_{14}O_3$, apparently quite free from by-products, was obtained. It is necessary to avoid diluting the oxalic acid solution too much, otherwise no separation of crystals occurs, the oxalate of the compound $C_{17}H_{15}NO_2$ appearing to be capable of existing in dilute solution. Aqueous acetic acid is capable of effecting the same transformation, but a considerable quantity of the substance is converted into phenanthraquinone. It is worthy of remark that formic acid, unlike acetic acid, causes the separation of the pure compound $C_{17}H_{14}O_3$ from the solution of the nitrogenous compound, no regeneration of phenanthraquinone occurring in this case.

The compound $C_{17}H_{14}O_3$ is insoluble in water; on heating with water separation of phenanthraquinone occurs, and this change takes place still more readily on warming with dilute caustic alkalis. Ether, alcohol, and acetone dissolve it freely. In alcoholic solution it is con-

verted by boiling into phenanthraquinone; but by avoiding a temperature above 40° it may be readily recrystallised from alcohol.

Action of Ammonia upon the Compound $C_{17}H_{14}O_3$.—On passing gaseous ammonia into the ethereal solution of the compound $C_{17}H_{14}O_3$, the rhomboidal laminæ of the compound $C_{17}H_{14}NO_2$ were deposited. These fused with decomposition at 130° , and were further identified by their behaviour towards concentrated hydrochloric acid, in which they dissolved, the solution becoming after a time green and turbid, and ultimately depositing the characteristic dark blue precipitate. This process of formation of the $C_{17}H_{14}NO_2$ is exactly the reverse of that which occurs in the formation of the compound $C_{17}H_{14}O_3$, and would therefore be expressed by the equation—



Action of Heat upon the Compound $C_{17}H_{14}O_3$.—About 0.5 gram of the substance was introduced into a narrow test-tube, which was then drawn out so as to form a retort. The neck of this retort was bent into U-shape. The retort was heated in a bath of sulphuric acid, and the bend was cooled by ice. The temperature was gradually raised to 190° . The substance fused, became darker in colour, and appeared to boil. As soon as this boiling ceased, the operation was interrupted. In the U-tube there had condensed about one drop of a colourless liquid, which had the characteristic odour of acetone, and which on exposure to the air rapidly evaporated, without leaving any residue. The substance in the retort solidified on cooling to a mass of dark orange-coloured needles, having the appearance of impure phenanthraquinone. They dissolved, with the exception of a trace of resinous matter, in hydrogen-sodium sulphite, and were precipitated of a bright orange colour on the addition of dilute sulphuric acid. The fusing point of the substance thus purified agreed exactly with that of phenanthraquinone.

The compound $C_{17}H_{14}O_3$ appears therefore to be decomposed by the action of heat into phenanthraquinone and acetone, according to the equation—



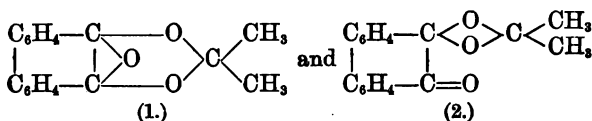
Synthesis of the Compound $C_{17}H_{14}O_3$ by the Direct Union of Phenanthraquinone and Acetone.—In order to ascertain whether the above process of decomposition could be reversed, and the compound $C_{17}H_{14}O_3$ produced by the direct union of phenanthraquinone and acetone, phenanthraquinone was heated with a large excess of pure acetone in sealed tubes. Nothing was formed up to 150° . After heating for four hours at 200° , the contents of the tubes appeared black and as if decomposed. The liquid portion was poured off from the

solid, and gently heated to drive off the acetone, when a pitchy mass was left. This was digested with a warm (not hot) solution of hydrogen sodium sulphite, in order to remove any unattacked quinone, and the residue, after washing with water, was dissolved in ether. The dark-coloured ethereal solution was shaken with freshly ignited animal charcoal, after which it appeared of a pale yellow colour, and by spontaneous evaporation deposited the characteristic straight blades of the compound $C_{17}H_{14}O_3$. These after recrystallisation fused at $88-89.5^\circ$.

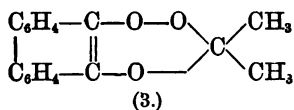
In presence of an excess of acetone the compound $C_{17}H_{14}O_3$ is therefore stable at a temperature above that at which it otherwise undergoes decomposition.

Acetic anhydride is without action upon the compound at ordinary temperatures, whilst at higher temperatures phenanthraquinone is regenerated.

Theoretical Considerations.—For the compound $C_{17}H_{14}O_3$ two formulæ might be suggested, which would account for its formation from phenanthraquinone and acetone, and its decomposition into these two substances—



A formula in which the two carbon-atoms, which in phenanthraquinone are united to quinonic oxygen, are represented as attached to each other by double bonds, appears to be inadmissible. The only such formula is—



and this, in addition to its inherent improbability, would not readily account for the formation of the compound $C_{17}H_{14}NO_2$.

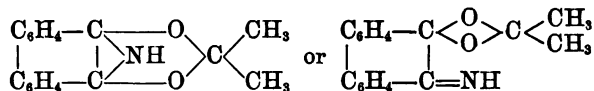
Various formulæ might of course be constructed, in which the phenylene groups or the methyl groups are represented as having undergone modification during the reaction, or in which the C_3 -group of the acetone is directly united to the phenanthrene nucleus; but such formulæ would fail to explain the ready decomposition of the substance into acetone and phenanthraquinone. Rejecting, therefore, these formulæ, the above three alone remain for discussion.

It might, however, be suggested that the compound is a so-called molecular combination of phenanthraquinone with acetone. This is, we think, very improbable. The compound fuses without decomposi-

tion more than 30° above the boiling point of acetone. Its mode of formation by the action of acids on the compound $C_{17}H_{15}NO_2$ also speaks very decidedly against this view. The compound $C_{17}H_{15}NO_2$ would, on this supposition, have to be regarded as a molecular combination of phenanthraquinonimide with acetone. But phenanthraquinonimide does not dissolve in hydrochloric acid, whereas the compound $C_{17}H_{15}NO_2$ is readily soluble.

We have above stated our belief that formula (3) must be rejected. Between formulæ (1) and (2) we are at present unable to decide, but we hope by a further study of the compound to clear up points that are still obscure. We refrain meanwhile from discussing the bearings of this reaction upon the formula of phenanthraquinone, beyond expressing the opinion that the reaction appears to render Graebe's formula somewhat improbable.*

The compound $C_{17}H_{15}NO_2$, which is formed by replacing O in the compound $C_{17}H_{14}O_3$ by NH, would receive the formula—

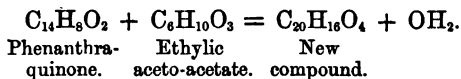


according as formula (1) or formula (2) is adopted for the compound $C_{17}H_{14}O_3$.

As regards nomenclature, it will, we think, be best to adopt for these compounds, provisionally at all events, names which express their mode of formation rather than their constitution. We propose to name the compound $C_{17}H_{14}O_3$, *acetonquin of phenanthrene*. Since the compound $C_{17}H_{15}NO_2$ is formed from the acetonquin by the substitution of NH for O, it will receive the name *acetonquinimide of phenanthrene*.

We intend to continue the study of these reactions, and if possible to apply them to other quinones and ketones, and to replace ammonia by amines. According to the above interpretation of the reactions, only primary amines ought to be capable of taking part in them.

We are also engaged in studying the action of ethylic aceto-acetate upon phenanthraquinone. The reaction is quite distinct from that which occurs with acetone. Instead of a direct union of the elements of ketone and quinone, combination occurs with elimination of water:—



The reaction is probably analogous to the condensations between

* This is certainly in direct opposition to the view frequently maintained by one of us in former communications.

ethylic aceto-acetate and aldehydes, described by Claisen (*Ber.*, 14, 345). Ethylic malonate may be expected to react with phenanthraquinone in a similar manner.

We trust that the study of these reactions will throw some light upon the constitution of phenanthraquinone.

XLII.—A Study of some of the Earth-metals contained in Samarskite.

By HENRY E. ROSCOE, V.P.R.S., President of the Manchester Literary and Philosophical Society.

THE probable existence of a new metal contained in samarskite from Mitchell County, North Carolina, was announced by Delafontaine in 1878 (*Ann. Chim. Phys.* [5], 14, 238). This discovery was confirmed by him shortly afterwards (*Compt. rend.*, 87, 559), and the name *Philippium* was given to the new metal. Its atomic weight was ascertained to lie between 123 and 126, and several of its salts were described (*Archives de Genève* [3], III, No. 3, March, 1880). Of these salts by far the most characteristic is the soluble formate depositing in well-defined rhombic crystals. Indeed this property of the new metal to yield a well crystallised formate is the only one, except its constant atomic weight, given by its discoverer as a means of distinguishing it from terbium or yttrium, or from a mixture of these two. In this respect, however, it differs distinctly from the two metals above mentioned which accompany it in samarskite, inasmuch as, under similar circumstances, the terbium formate is deposited as a white powder, whilst the corresponding yttrium salt is very much more soluble, and usually forms a deliquescent mass.

Although this property of the differing solubilities of the formates affords by far the best means known of separating the three metals in question, still even this method does not yield satisfactory results, as is pointed out by Delafontaine (*Compt. rend.*, 87, 560): "On n'a encore aucun moyen de reconnaître si la philippine est complètement débarrassée d'yttria, quoiqu'il soit facile de réduire beaucoup la proportion de cette dernière." The different solubility of the sulphates in a saturated solution of potassium sulphate does indeed serve for the separation of the rare earth-metals into two or more groups, and has been generally adopted as a method for this purpose, but it cannot be used for isolating the closely allied individual members of these groups. Moreover, Bunsen's process of separation, depending upon

the varying stability of the nitrates at high temperatures, has been shown by Marignac to be unavailing in the case of the samarskite earths (yttria and terbia), although yielding more satisfactory results with the gadolinite earths (yttria and erbia).

The processes adopted for the preparation of the earths from the mineral, and for their purification and separation in the present instance, were briefly as follows:—About 1500 grams of coarsely powdered samarskite was treated, 100 grams at once, in a large platinum dish with a quarter of a litre of commercial hydrofluoric acid diluted with about its own bulk of water (L. J. Smith, *Compt. rend.*, **87**, 146). When the effervescence accompanying the decomposition had ceased, the whole was brought to boiling, and another 100 grams of the mineral added little by little, and the mass then heated to expel some of the excess of hydrofluoric acid. The solution, containing iron, niobium, tantalum, &c., was then decanted from the greenish precipitate, and this was well washed, dried, and heated with an excess of sulphuric acid; the sulphates were then dissolved in water, and the uranium was oxidised by addition of nitric acid and subsequent boiling. From this solution the earths were thrown down by ammonium oxalate. The oxides obtained by the ignition of the oxalates were then converted into nitrates, and these were fused, so as to decompose thorium salts as well as remaining traces of iron (Nilson, *Ber.*, 1880, p. 1430). On exhausting the small quantity of brown insoluble residue with water, the filtered solution was precipitated with powdered potassium sulphate. The oxides in the precipitate, and those remaining in solution, were severally converted into neutral sulphates, and by a series of fractional precipitations with potassium sulphate, these were separated into two portions (Marignac). One of these yielded a sulphate soluble in 30 parts of a cold saturated solution of potassium sulphate, and gave an oxide having a fawn colour: the other gave a sulphate insoluble in 200 parts of the above solution, and yielded an oxide having a brown colour. The first portion of oxides should consist of philippium, yttrium, terbia, and traces of erbia; it weighed about 60 grams. The second should contain didymium, decipium, yttrium β , &c. This portion weighed about 25 grams. It is with the separation of the metals contained in the first portion that we are at present concerned.

For this purpose the oxides were converted into formates, and these submitted to a long-continued and systematic series of fractional precipitations. This was accomplished, in the first place, by exhausting the dried and powdered formates fractionally with hot water, and secondly, by partially precipitating the aqueous solution of the formates by addition of alcohol. The first method was employed with oxides whose atomic weight approximated to that of yttrium ($Y_{tt} = 88.5$), the

second with those whose atomic weight more nearly approached that of terbium ($Tb = 147$).

This method of fractional treatment of the formate was repeated on the 60 grams of oxide very many times, the plan generally adopted being that of extracting the powdered mass with small volumes of hot water, each extract being then evaporated to dryness and analysed. The residues obtained by this evaporation were then treated in a similar way, and the portions of the several extracts which showed close approximation in composition were mixed together, and the mixture treated as above, this process of fractionation and mixing being pushed as far as was found possible. The following tabular statement of some few of the earlier operations may serve to explain the process adopted:—

Operation A.

	Weight of oxide. grams.	Percentage of oxide in-formate.	
Fraction 1	3.41	61.1	
„ 2	7.10	58.2	} united and used in operation B.
„ 3	7.44	57.1	
„ 4	6.05	54.1	
„ 5	8.67	52.9	} united and used in operation C.
„ 6	4.00	52.4	
„ 7	9.33	51.6	
Total	46.00		

Operation B.

Fraction 1	6.32	54.2
„ 2	4.69	56.6
„ 3	3.60	61.2
Total	14.61	

Operation C.

Fraction 1	7.07	50.9
„ 2	12.59	53.9
„ 3	2.00	59.5
Total	21.66	

Of these the following, either singly or mixed together, were subjected to further treatment:—

	Grams.	
$A_1 + B_3 =$	7.01	(used in operation D).
$A_4 + B_1 + C_2 =$	24.96	„ E).
$B_2 =$	4.69	„ F).
$C_1 =$	7.07	„ G).

By a systematic repetition of these processes a separation was effected into a large number of fractions, one of which was richest in terbia; another intermediate portion, which was richest in so-called philippia, and another richest in yttria.

It is scarcely necessary to remark that in these experiments the determination of the atomic weight of the several mixtures of oxides is a matter of the greatest consequence, as this is the only trustworthy means of ascertaining how the process of purification is proceeding. A long series of estimations showed that atomic-weight determinations founded upon the incineration of the formates, yielded even less satisfactory results than had previously been reported by Marignac (*Archiv. Gen.*, III, No. 5, pp. 11, 13), so much so, that this method was discarded for the ordinary and perfectly trustworthy sulphuric acid determination. The reasons which led to the abandonment of the formate process were the difficulty of obtaining formates of constant composition, even when the conditions of preparation were kept as similar as possible, and also the fact that on repeatedly extracting the formate with small quantities of hot water the residual salt becomes basic.

The intermediate fractions of oxides, above referred to, weighing 8.83 grams, and exhibiting an atomic weight, by sulphuric acid process, of (121), was next repeatedly fractionated by partial precipitation of the formate solution with alcohol, the atomic weight of each precipitate being determined. Thus the two fractions containing the least soluble formates, weighing 0.98 gram, gave an atomic weight of 130—145. The middle portions, consisting of three fractions, weighing 5.32 grams, gave an atomic weight of 121.8—123. The most soluble portions, consisting of three fractions, weighing 1.4 gram, gave an atomic weight of 107—117.

The intermediate portion of 5.32 grams was again submitted to a repetition of the same treatment, and was divided by fractional precipitation into four portions of oxide:—No. 1, weighing 0.9, had an atomic weight of 132; No. 2, weighing 2.96, had an atomic weight of 123; No. 3, weighing 1.07, had an atomic weight of 114.7; No. 4, weighing 0.4, had an atomic weight of 111.9. It is thus clear that all attempts to obtain a formate possessing a constant atomic weight of 121—123 failed, a material possessing the above composition being incapable of yielding a homogeneous series of fractionations, but giving rise to products of widely differing atomic weight.

This result coincides with that obtained by Marignac (*Archiv.* [3], III, No. 1, May, 1880), who, confining his attention to the samarskite oxides whose nitrates are most stable, says, respecting this process of separation: "Comme autre moyen de séparation, j'ai eu recours au procédé, recommandé par M. Delafontaine, fondé sur la différence de

solubilité des formates. Par l'emploi de cette méthode je n'ai pu y constater que la présence de deux terres déjà connues, l'yttria et la terbina." In the present investigation the separation of the earths according to Bunsen's process of partial decomposition of the nitrates, was not used, so that the whole of these earthy oxides, that is yttria, philippia, and terbia, contained in the mineral, were passed through the processes of fractionation, and amongst these no oxide having an unalterable atomic weight of 122 could be detected.

Nevertheless, the remarkable fact remains, and demands explanation, that the formate yielding an atomic weight of about 122 possesses distinctly different physical characters from the formates obtained from oxides of either much higher or much lower atomic weight. The following description of these bright glassy well-defined rhombic prisms, often many millimeters in length, may serve for their identification:—

System rhombic. Forms ∞P , $P\infty$ and $P\infty$.

$$a : b : c = 0.890 : 1 : 1.484.$$

$$\infty P : \infty P \text{ (brachydiag.)} \dots 82^\circ 52'.$$

$$\text{Ditto (macrodiag.)} \dots 97^\circ 10'.$$

$$P\infty : P\infty \text{ (summit)} \dots 67^\circ 30'.$$

$$P\infty : P\infty \text{ (ditto)} \dots 61^\circ 57'.$$

One possible explanation of the formation of these crystals is that they may consist of a mixture of the higher and lower formates, possessing the property of crystallising as a kind of double salt. To ascertain how far this supposition is correct, the following experiments were made:—

Three grams of crude yttria, obtained by the fractionation processes above described, and having an atomic weight of 101.4, and 3 grams of crude terbia prepared in the same way, and having an atomic weight of 147.9, were each converted into formates. Of each of these formates two-thirds was brought into solution separately, whilst the other third of the terbia was mixed with the remaining third of the yttria. Thus three solutions were obtained: (A) contained 2 grams of crude terbia, (B) contained a mixture of 1 gram of crude terbia with 1 gram of crude yttria, and (C) contained 2 grams of crude yttria. The terbia (A) required 130 c.c. of water for solution; the mixture (B) required 44 c.c. for solution, and the yttria (C), which dissolved in much less water, was diluted with water, so as to make up 44 c.c. of solution. To each of these three solutions an equal bulk of alcohol was added, the liquids being then allowed to stand for the same length of time.

Solution A yielded (1) a pulverulent precipitate burning on incineration with showers of sparks; the weight of the constituent

oxides was 1.125, having an atomic weight of 149.1; and (2) a mother-liquor containing 0.720 of oxide with an atomic weight of 142.3.

Solution B yielded (1) a deposit crystallising in rhombic prisms, which could not be distinguished from similar crystals obtained in the previous operations from an oxide having an atomic weight of about 122; these did not burn on incineration with showers of sparks; the weight of the oxides contained in these crystals was 0.959, with an atomic weight of 127.2; and (2) a mother-liquor containing 0.905 of oxide with an atomic weight of 114.3.

Solution C yielded (1) a crystalline deposit weighing 0.675, with an atomic weight of 104.6; and (2) a mother-liquor containing 1.255 of oxide, with an atomic weight of 101.8.

These results prove that the formates of terbium and yttrium are capable of crystallising together in a form ascribed to philippium: for solution (B), although containing 1 gram of terbia dissolved in 44 c.c. of water, deposited only a trace of a pulverulent formate in place of at least 0.5 gram, which must have been thrown down if the terbia present had behaved as it does when alone in solution. But the above numbers also show that the quantity of crystals yielding 0.950 gram of oxide having an atomic weight of 127.2, is larger than could be obtained from the amount of philippia, supposing such a substance to exist, which could possibly be present in either of the materials employed. Thus the 1 gram of crude terbia might possibly contain 0.108 of philippia ($Pp = 125$), whilst the 1 gram of crude yttria might contain 0.202 of philippia. Hence the total weight of philippia which could be obtained in the form of a crystalline formate is 0.310, whereas in fact more than three times this quantity, viz., 0.959 (atomic weight 127.2) was found.

If the oxide of philippia was analogous to the other rare earths, a sesquioxide R_2O_3 , the atomic weight would be = 122—126; but an element with such an atomic weight could not find its place in the periodic system of elements.

My best thanks are due to Mr. Harry Baker, Berkeley Fellow of the Owens College, for the able and unwearied assistance which he has given in carrying out the above experiments.

Spectroscopic Examination.—One of the characteristic properties originally ascribed by Delafontaine to philippium is the existence of a distinct broad absorption-band to which he gives the wave-length of 450 (*Compt. rend.*, **87**, 561). He, however, withdraws this statement in a subsequent communication (*Archiv.* [3], **3**, 15), and Soret (*Archiv.* [3], **4**, 80), confirms this view by stating that no visible absorption-band characterises this metal, and that the above-mentioned absorption-band is due to holmium.

XLIII.—*The Spectrum of Terbium.*

By H. E. ROSCOE and A. SCHUSTER.

TWO methods for obtaining the spectrum of terbium were used. The first was that of Bunsen (*Pogg. Ann.*, 155, 230, 1875, and *Phil. Mag.* [4], 50, 416, 1875), in which the spark is taken from pointed poles of charcoal saturated with a liquid solution of the metal. When however, as in the present instance, a good spectrum can be obtained only by means of a very strong spark, the method has some disadvantages. The carbon poles burn away very quickly, and have to be renewed constantly; the spark also is very unsteady. In a great part of the experiments therefore, a second method was employed, in which the spark was simply taken in a small glass tube from the liquid solution.

The spectrum of terbium is at its best very weak, though it contains a great number of lines. The lines of yttrium present as an impurity are stronger than the strongest terbium lines.

A large grating of Mr. Rutherford, containing 17,290 lines to the inch, was used, and all measurements were taken in the spectrum of the second order. The focal length of the observing telescope was 17.4 inches. The measurements were taken by means of a micrometer eyepiece, the screw of which had 100 turns to the inch.

It is difficult to form a very definite idea as to the probable accuracy of the numbers given in the table; but the close agreement of different measurements renders it improbable that an error of 0.5-tenth meter will often occur, except perhaps in the weakest lines; the position of which in some cases had almost to be guessed at. In order to see what degree of accuracy could be obtained with the dispersion employed under favourable conditions, the wave-lengths of some known iron lines were interpolated between others in the same way in which the terbium lines had been determined. Thus, for instance, an iron line given by Ångström as 5017.62 was determined on one day as 5017.76, and on another as 5017.89. Another line found by Ångström to be 4956.73 was on two successive days measured as 4956.76 and 4957.09.

In the subjoined list the intensities are marked by means of numbers, 1 being the highest and 7 the lowest intensity; but these numbers must be considered as only approximate. In the first place the relative intensities are not invariable, but may alter with the strength of the spark; and even with one and the same spark, two lines may reverse their relative intensity according as the centre or the edge of the spark is observed. Then, again, it is almost impossible to com-

pare the intensity of a violet and a green line, especially when they cannot be brought together into the same field of view. The difficulty is increased by the fact that the continuous spectrum forming the background on which the lines are seen, may be strong in some parts and weak in others. It is nevertheless desirable to add a column for the relative intensities, for even if the numbers are not to be trusted for lines which are situated in different parts of the spectrum, the characteristic groups of closely adjoining lines which are often seen, generally preserve their character as far as relative intensities are concerned; and such groups often serve as a better test for the presence of an element, than the measurements of a few strong lines.

The spectrum of terbium, as will be seen from the table, begins in the green at a point somewhat less refrangible than E. A few lines still less refrangible could be seen, but their weakness prevented any satisfactory measurement. No lines were observed in the yellow and red, except lines belonging to yttrium, which were of course carefully eliminated throughout the spectrum.

The specimen of oxide which ought to contain philippium in large quantities, should that element exist, showed, with one exception, only lines which could be traced either to yttrium or to terbium. The one exception is a line nearly coincident with the iron line 4956.7 (\AA). The line cannot be due to iron, as the lines which first appear when iron is present as an impurity could not be seen, and a careful examination rendered it probable that the coincidence is not an absolute one. This line is present both in terbium and in yttrium, but it is undoubtedly stronger in the so-called philippium. It is not to be confounded with a terbium line which is very near to it. We have tried to see whether a mechanical mixture of terbium and yttrium would bring the line out to any marked degree. Owing to the great number of terbium lines in the neighbourhood, no decided result could be obtained, but our impression was, that such a mixture did not bring out the line.

Although one cannot explain the existence of this line, which is apparently not due to any known element the spectrum of which has been accurately measured, but which may possibly belong to holmium or thulium, we do not consider that the existence of this single line, which seems to be more brilliant in the so-called philippium, is sufficient spectroscopic evidence for the existence of this element. The spectra of all the metals of the same chemical group contain a large number of lines. Thus we have mapped close on 200 terbium lines; and it is to be expected that did an element like philippium exist, it would make its presence apparent by more than one line. As an example of the great caution necessary in these investigations, we may mention that a platinum line due to the pole came out repeatedly more

strongly in the philippium than either in terbium or yttrium, so that had we not proved it to be a platinum line by its disappearance when carbon poles were used, it might easily have been ascribed to philippium.

The oxides employed in the above experiments were (1), the terbia used for solution A, described in the preceding paper, having an atomic weight of 147·9; (2), the intermediate oxides supposed to contain philippia, having an atomic weight of 121·8—123; (3), the yttria used for solution C, and having an atomic weight of 101·4.

The above specimen of terbia gave a faint absorption-spectrum of didymium, corresponding to about 4 per cent. of this latter. The intermediate oxide and the yttria showed about as strongly the absorption lines of erbium and holmium.

Wave-length.	Intensity.	Remarks.	Wave-length.	Intensity.	Remarks.
5371·4	2	Stronger at pole than in centre of spark.	5190·3	2	
5369·4	4		85·8	2	
5368·3	4		82·8	3	
5367·2	2		75·4	1	
5360·3	4		74·6	1	
5352·1	3		72·3	1	
5349·6	1		65·6	5	
5347·7	3		55·2	3	
5342·3	2		54·4	4	
5340·0	3		40·5	6	
5331·4	6	Weak and uncertain.	29·8	4	Weak and uncertain.
5320·5	1		24·9	6	
5318·7	1		21·5	5	
5306·4	1		16·5	4	
5301·6	1		11·8	7	
5300·6	1		08·5	4	
5292·3	5		04·2	5	
5281·6	2		02·9	3	
5280·4	2		5100·1	1	Very weak.
5271·9	5	Intensity variable according to strength of the spark.	5097·8	4	
5270·6	1		91·9	3	
5268·8	2		73·9	4	
5264·5	6		70·7	2	
5261·4	6		69·2	2	
5254·8	3		66·5	5	
5251·1	1		60·6	6	
5250·1	3		57·2	4	
5248·6	4		52·3	2	
5236·7	5	Measurement uncertain.	50·9	6	
5233·3	4		30·4	2	Very weak.
5232·0	5		27·9	2	
5218·7	3		5014·6	2	
5197·1	2		4960·9	2	
5195·1	5		56·6	3	
92·0	2		4951·7	3	
			47·6	2	
			37·1	4	

Wave-length.	Intensity.	Remarks.	Wave-length.	Intensity.	Remarks.
4935.5	4		4553.5	5	
33.1	6		52.4	5	
11.9	6		43.6	3	
4909.0	5		41.3	4	
4893.2	6	Double.	39.5	3	Intensity variable.
64.2	6		37.2	2	Do. do.
47.0	3		23.6	3	
43.7	6		22.7	4	
41.2	6		21.9	6	Weak and uncertain.
21.1	5		19.2	3	
4815.0	1		11.5	4	
4799.8	4		4498.7	4	
90.2	4		97.6	5	
81.9	6		96.9	4	
76.7	5		83.9	6	
73.6	6		82.8	5	
66.1	5		80.6	5	
57.6	6		75.9	6	
54.5	6		73.4	6	Double.
44.8	2		72.2	4	
43.0	5		70.9	5	
25.4	6		66.9	1	
20.0	6		66.1	6	
17.0	6	Both these lines probably close doubles.	62.6	6	
15.0	6		58.3	3	
12.0	4		54.3	2	
03.5	2		52.6	2	
00.2	2		49.6	6	
4686.5	4		44.0	4	
76.1	3		41.8	6	
		There is an Yt line at 4673.8 which is decidedly less refrangible.	37.8	5	
73.6	3		35.6	4	Broad.
			35.1	4	
68.6	2		33.7	1	
54.5	5		30.1	6	
46.4	6		27.3	6	
41.6	3		23.8	2	
38.0	5		20.6	5	
35.9	6		20.3	5	
14.9	3		18.7	5	
03.5	6		14.3	4	
00.3	4	Weak and doubtful.	08.9	5	
4597.3	6		07.7	5	
96.3	6		06.3	4	
94.3	5		02.7	6	
93.0	5		01.4	6	
90.8	6	Weak and doubtful.	4390.4	3	
89.0	6	Do. do.	87.1	6	
84.1	4		82.4	6	
81.7	4		80.1	6	
80.5	6		73.4	5	
76.9	3		69.2	3	
65.7	3		61.4	4	
60.3	6	Weak and doubtful.	60.4	3	
57.6	6	Do. do.	51.6	6	
			50.2	6	

Wave-length.	Intensity.	Remarks.	Wave-length.	Intensity.	Remarks.
4347·1	2	<div style="display: inline-block; vertical-align: middle;"> <div style="font-size: 3em; vertical-align: middle; margin-right: 5px;">{</div> Has a more refrangible companion. Weak and uncertain. </div>	4328·4	4	Double. Do.
46·0	4		26·1	5	
41·7	2		25·0	4	
35·5	6		18·4	3	
33·4	3		15·3	6	
29·8	6		13·1	6	
			08·7	5	

XLIV.—*On the Behaviour of Zinc, Magnesium, and Iron as Reducing Agents with Acidulated Solutions of Ferric Salts.*

By T. E. THORPE, F.R.S.

WHEN a piece of zinc, or magnesium, or iron, is thrown into a solution of a ferric salt acidulated with sulphuric acid or hydrochloric acid, more or less hydrogen is evolved, and more or less of the iron salt is reduced to a lower state of oxidation. The extent of the reduction with a given weight of the metal, and for a particular strength of the solution, varies, with the two first named metals at least, inversely as the amount of hydrogen evolved: if we knew the quantity of the hydrogen which would be evolved by the solution of the metal in the pure acid—a matter of simple calculation—we could ascertain the degree of reduction from the diminished volume of the hydrogen formed on adding the metal to the acidulated ferric solution; or, which of course comes to the same thing, we could in the case of the magnesium and zinc ascertain the amount of the *retained* hydrogen by determining the quantity of the ferrous salt, by the aid of one of the well known volumetric processes.

The extent of the reduction of the ferric salt must depend upon a number of circumstances. It may vary with the strength of the solution, with its temperature, with the amount of free acid present, and lastly, with the specific nature of the metal employed. The problem, which is to determine the conditions under which the nascent hydrogen does work as a reducing agent, is obviously very complex, and the present communication can be regarded only as an instalment towards the complete solution of a question in chemical dynamics which offers features of considerable theoretical interest, and some of no little practical importance.

My method of experiment was as follows:—I first prepared a solution of ferric sulphate by dissolving precipitated and well washed ferric

hydrate in sulphuric acid, and diluting the liquid until each cubic centimeter contained 0.009544 gram of iron and 0.03359 gram SO_4 ; of this 0.02527 was calculated to be combined with the iron, forming ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, leaving 0.009228 gram of free sulphuric acid (H_2SO_4). I next made a solution of sulphuric acid, of which 1 c.c. contained 0.1912 gram H_2SO_4 . 25 c.c. of the iron solution, containing 0.2386 gram iron, and 25 c.c. of the dilute sulphuric acid, containing 4.78 gram H_2SO_4 , were placed in a wide test-tube of about 100 c.c. capacity, standing in a water-bath, and so arranged that whilst it could be heated to any determinate temperature, the liquid within it could be kept in continual and rapid agitation during the evolution of the hydrogen. The metal employed was in the form of thin sheet or foil, and was fastened to a tube in such a manner that it could be entirely immersed whilst the liquid had ready access to its surface. In order to prevent the possibility of the reoxidation of the reduced iron by atmospheric oxygen, a current of carbonic acid or coal-gas was passed into the upper part of the test-tube. The iron solution was first heated to the requisite temperature by a sufficiently prolonged immersion in the water-bath, and the weighed and measured quantity of the metal was lowered into it, and the apparatus set in agitation. On the completion of the evolution of the hydrogen (the duration of which was noticed), the amount of reduced iron, and thence of retained hydrogen, was estimated by a permanganate solution of known strength.

Experiments were made with zinc, magnesium, and iron.

I. Zinc.

A rectangular piece of zinc-foil, weighing 0.3116 gram, and measuring 40×30 mm., was immersed in the solution containing 0.8704 gram $\text{Fe}_2(\text{SO}_4)_3$ and 5.01 grams free H_2SO_4 , at the ordinary temperature of the air. The time of solution was 42 minutes. On titration the solution required 11.55 c.c. of permanganate (1 c.c. = 0.000191 gram H). Hence the amount of hydrogen retained, that is, which had done work in reduction, was 23.1 per cent. of the quantity which would have been evolved by the action of pure sulphuric acid. A similar experiment, in which 0.3206 gram of zinc was used, requiring 47 minutes for solution, gave 22.6 per cent. Hence we may say, that three-fourths of the hydrogen escaped without exercising any reducing action in a solution containing $1\frac{1}{2}$ per cent. of ferric sulphate and 10 per cent. free sulphuric acid, at the ordinary temperature of the air.

I then studied, one by one, the effect of the various circumstances which could modify the reducing action effected by the metal in the act of solution.

1. Temperature. 0.8704 gram $\text{Fe}_2(\text{SO}_4)_3$ and 5.01 grams free H_2SO_4 employed in each experiment. Care was taken to maintain the solution at the required temperature during the solution of the metal. The area of the zinc was 40×30 mm.: its thickness was 0.038 mm.

Temperature.	No. of experiments.	Mean weight of zinc used (thickness 0.038 mm.).	Mean time of solution (minutes).	Per cent. of hydrogen retained (mean).
6—7°	3	0.3124	80	22.0
10	2	0.3483	70	23.0
16—17	5	0.3357	46	23.6
25	10	0.3297	43	26.7
35	6	0.2996	35	27.2
55	5	0.3182	29	27.5
75	2	0.3113	16	30.5
96—97	5	0.3122	12	33.8

These results are graphically represented by the curve A in the accompanying diagram: the abscissæ represent the percentage amounts of hydrogen retained, and the ordinates the temperatures.

The pieces of zinc employed had a thickness of 0.038 mm.: it becomes of importance to determine if the amount of the reduction is influenced by the extent of surface of metal exposed. A second series of experiments was therefore instituted with the same weight of sheet zinc of a thickness of 0.115 mm., that is, three times the thickness of that used in the first series. The results are contained in the following table, and are graphically represented by the curve B.

Temperature.	No. of experiments.	Weight of zinc used (thickness 0.115 mm.).	Time of solution (minutes).	Per cent. of hydrogen retained.
15°	1	0.3220	80	17.9
25	1	0.3192	58	18.5
30—31	2	0.3425	52	19.8
50—52	2	0.3217	34	22.3
75	2	0.3329	20	24.7
98—99	3	0.3081	12	28.1

It follows from these observations that the extent of the reduction effected by a given weight of the zinc in the act of dissolving increases with the temperature. It is also affected, although to a much less degree, by the relative extent of surface of metal exposed. The observations are far too few in number to permit any certain conclusions to be drawn with respect to the connection between the amount of reduction and the initial surface of metal.

The time of solution of the zinc varied from as long as 80 minutes to as little as 12 minutes; it becomes of interest to determine if the

rapidity of the evolution of the hydrogen affects the extent of the reduction. The rate at which the hydrogen is evolved may be varied by altering the amount of free acid. A series of experiments was therefore made, in which the amount of free acid and the temperature were the only variables. The temperatures chosen were 25° and 97°. Thickness of zinc 0.038 mm.

With 5.01 grams free H_2SO_4 .

Temp.	No. of experiments.	Weight of zinc.	Time of solution.	Per cent. of hydrogen retained.	Per cent. hydrogen. Time.
25°	10	0.3297	43	26.7	0.62
97	5	0.3122	12	33.8	2.82

With 2.14 grams free H_2SO_4 .

25	2	0.3237	61	32.9	0.54
97	2	0.3199	15	39.4	2.62

With 1.19 grams free H_2SO_4 .

25	2	0.3307	82	34.7	0.42
97	2	0.3203	18	41.7	2.32

It will be seen that whilst the extent of the reduction, as well as the rapidity of the solution, increases with the temperature; at a given temperature the extent of the reduction increases, although at a gradually diminishing rate with the time of solution.

The presence of dissolved zinc sulphate exercises a slight retarding effect upon the extent of reduction, whilst it also slightly shortens the time of solution.

0.8704 gram $\text{Fe}_2(\text{SO}_4)_3$ + 5.01 grams sulphuric acid. Vol. of sol. = 50 c.c.

Temp.	Weight of zinc.	Time of solution.	Per cent. hydrogen retained.
97°	0.3122	12 min.	33.8

0.8704 $\text{Fe}_2(\text{SO}_4)_3$ + 5.01 grams SO_4H_2 + 1 gram $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. (Vol. of sol. = 50 c.c.)

98	0.3331	9 min.	29.9
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0.8704 $\text{Fe}_2(\text{SO}_4)_3$ + 5.01 gram SO_4H_2 + 1 gram ZnSO_4 (anhydrous.)

97	0.3319	10 min.	29.7
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0.8704 $\text{Fe}_2(\text{SO}_4)_3$ + 5.01 gram SO_4H_2 + 5 grams ZnSO_4 .

99	0.3366	9 min.	28.2
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The rapidity of the solution and also the extent of the reduction effected by a given quantity of zinc of a determinate area, in a solution

of a given temperature containing a definite weight of the acid, increases with the amount of reducible iron present. This is shown by the following experiments, made at 25° and 97°:—

Ferric sulphate 0·8704 gram + 5·01 grams sulphuric acid. (Vol. = 50 c.c.)

Temp.	Weight of zinc.	Time of solution.	Per cent. of hydrogen retained.	Per cent. hydrogen. Time.
25°	0·3297	43 min.	26·7	0·62
97	0·3122	12 „	33·8	2·82

Ferric sulphate 4·352 grams + 5·01 grams sulphuric acid. (Vol. = 50 c.c.)

25	0·3248	23 min.	62·8	2·9
97	0·3311	5 „	82·3	16·4

The quantity of iron present in the strong solution was five times the amount of that present in the weaker solution: the ratios of quotients obtained by dividing the times of solution into the amount of reduction, are also approximately as 1 to 5.

It results then from these observations that, provided there is sufficient acid present to dissolve the zinc, the maximum reducing action possible with a given weight of the metal is obtained by concentrating the ferric sulphate solution and diminishing the amount of free acid: the effect of concentration is to multiply the chances of contact of the hydrogen and the ferric sulphate molecules; increase of temperature brings about the same result, by augmenting the molecular movement within the liquid.

It is well known that the rapidity of the solution of the zinc in dilute sulphuric acid is increased by placing the zinc in contact with the more electronegative metals copper and platinum. Experiments were therefore made with zinc and platinum, to determine how far the metals in contact affected the reducing action of the evolved hydrogen. A piece of thin (No. 36) platinum wire, 32½ cm. long, was therefore wound round the weighed portion of zinc.

The results are as follows: (thickness of zinc 0·038 mm.).

Without Platinum.

Temperature.	Weight of zinc.	Time of solution.	Hydrogen retained.
25·36	0·3282	43 min.	25·9 per cent.
25·26	0·3308	46 „	26·2 „
55·0	0·3212	30 „	27·4 „
55·0	0·3078	29 „	26·7 „
96·0	0·3134	11 „	32·9 „
94·95	0·3064	14 „	33·1 „

With Platinum.

25.26	0.3243	31 min.	24.4 per cent.
25.26	0.3331	31 "	24.3 "
55.0	0.3282	19 "	24.8 "
55.0	0.3440	19.5 "	24.6 "
98.0	0.3198	9 "	31.5 "
98.99	0.3339	9 "	31.3 "

These results are graphically represented by the curve C.

Although the time of solution of the zinc in contact with the platinum is considerably diminished, as compared with that of the zinc alone, very little difference in the reducing effect is observed. It scarcely exceeds 2 per cent., and may possibly be wholly due to the platinum preventing the free contact of the ferric sulphate with the zinc. It would seem then that with a given quantity of zinc and free acid, the amount of active hydrogen formed is constant, and is independent of the rate of solution.

II. Magnesium.

The metal employed was in the form of ribbon, and was about 0.16 mm. thick; an amount which would evolve the same quantity of hydrogen as that afforded by the mean amount of zinc used in the foregoing experiments would weigh 0.1192 gram. The time of solution was in all cases exceedingly short, and can only be considered as approximately accurate. The results at various temperatures are as follows:—

Temp.	Weight of Mg.	Time of solution.	Per cent. of hydrogen retained.	Mean.
15°	0.1189	1 min.	5.98	
15	0.1183	1.2 "	5.89	
15	0.1071	1 "	5.99	5.95
25	0.1085	1 "	6.44	
25	0.1096	1 "	6.59	6.51
35	0.1119	1 "	6.92	
35.5	0.1054	1 "	7.07	6.99
49.5	0.1111	45 secs.	7.12	
49.5	0.1097	45 "	7.42	
50	0.1105	45 "	7.47	7.33
75	0.1107	45 "	7.46	
75	0.1087	45 "	7.38	7.42
98	0.1098	30 "	7.41	

These results, which are graphically represented by the curve, show that the reducing action exerted by magnesium is scarcely a fourth of that of zinc; in spite of the most rapid agitation of the liquid, comparatively little of the ferric salt becomes deoxidised.

Influence of Free Acid.—As in the case of the zinc, by decreasing the initial quantity of free sulphuric acid present, the reducing action is augmented. Thus with 5.01 grams H_2SO_4 —

Temp.	Weight of Mg.	Time of solution.	Per cent. of hydrogen retained.	Mean.
25°	0.1085	1 min.	6.44	
25	0.1096	1 „	6.59	6.51
98	0.1098	30 secs.	7.41	

With 2.14 grams H_2SO_4 —

25.26	0.1104	6 min.	9.85	
25.26	0.1103	6 „	9.87	9.86
96	0.1099	1.2 „	11.99	
98	0.1170	1.2 „	11.55	11.77

With 1.19 grams H_2SO_4 —

25	0.1111	37 „	11.77	
25	0.1093	40 „	11.74	11.76

In these cases the amount of reduction is only from $\frac{1}{4}$ to $\frac{1}{3}$ of that affected by the zinc under corresponding conditions. It will be seen, however, that the diminution of the rate of solution with the decrease in the amount of free acid present, is far greater in the case of magnesium than in that of zinc.

In the case of the zinc the rates are approximately in the ratios of

$$1 : 1\frac{1}{2} : 2.$$

In that of the magnesium they are

$$1 : 6 : 36.$$

This opens up a question which has been in part studied by Kajander (*Bull. Soc. Chim.* [2], 34, 325), who has already shown that the weight of magnesium dissolved in the unit of time by a given acid is a simple function of its concentration, and of the nature of the medium (water, saline solutions, &c.) in which the reaction is effected.

The effect of diluting the iron solution in the case of magnesium is exactly the same as in that of the zinc. A solution containing less than 0.5 per cent. of iron is practically unreduced by magnesium; the solu-

tion becomes solid from the formation of Epsom salts, before the whole of the iron is converted into ferrous salt.

In contact with platinum the reducing power of magnesium is but very slightly augmented, as the following experiments show. The conditions were precisely the same as in the observations with zinc, the same piece of platinum wire being used. No perceptible difference in the rate of solution could be observed.

With Platinum.

Temp.	Mg used.	Time of solution.	Hydrogen retained.	Mean.
25°	0.1070	1 min.	6.85	
26	0.1108	1 „	6.72	6.78
50	0.1107	45 „	7.66	
50	0.1100	45 „	7.80	7.73
75—76	0.1102	45 „	7.90	
75—76	0.1093	45 „	8.07	7.98
98	0.1115	30 secs.	8.43	
98	0.1108	30 „	8.28	8.35

As will be seen on inspection of the curve E which graphically represents these results, they differ but very slightly from those obtained in the absence of the platinum.

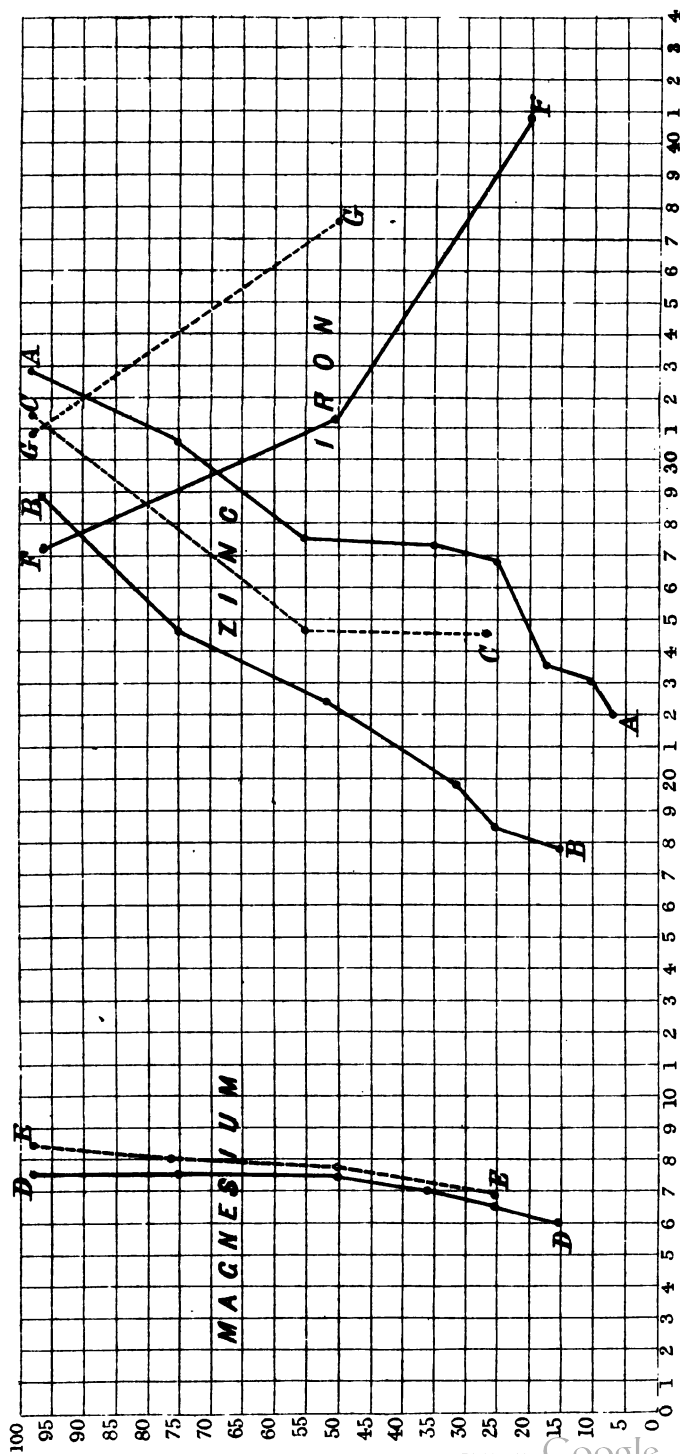
III. *Iron.*

The results of the experiments with this metal are altogether dissimilar to those with zinc and magnesium, inasmuch as with iron the rate of solution is extremely slow, and the reducing action *apparently* decreases with the temperature. The metal employed was the thinnest ferrotype iron procurable; it had a thickness of 0.158 mm. The amount equivalent to that of the zinc used in the foregoing experiments weighed 0.2468 gram. The quantity of the permanganate required by the solution of a known weight of the iron employed was ascertained in the first instance; the proportionate amount was then readily calculated and subtracted from the volume used in the determination of its reducing power. The results are as follows:—

0.8704 gram $\text{Fe}_2(\text{SO}_4)_3$ and 5.01 grams H_2SO_4 . Vol. = 50 c.c.

Temp.	Fe used.	Time of solution.	Hydrogen retained.	Mean.
20—35°	0.2666	1½ days	40.7	
50—52	0.2541	180 min.	32.5	
50—52	0.2565	190 „	30.7	
50—51	0.2635	190 „	30.5	31.2
96	0.2497	38 „	27.9	
96	0.2675	38 „	26.8	
96	0.2463	37 „	27.0	27.2

CURVES SHOWING REDUCING POWERS OF DIFFERENT METALS.



HYDROGEN RETAINED.

UNIVERSITY OF MICHIGAN

In contact with platinum both the rate of solution and the reducing action are increased; the action is *decreased*, however, on warming the liquid.

0.8704 gram $\text{Fe}_2(\text{SO}_4)_3$ + 5.01 grams H_2SO_4 . Vol. = 50 c.c.

With Platinum.

Temp.	Wt. of iron.	Time of solution.	Hydrogen retained.	Mean.
49—51°	0.2618	168 mins.	37.5	
98	0.2668	25 "	30.1	
98	0.2531	26 "	30.4	
98	0.2588	26 "	32.6	31.0

These observations are graphically represented by the curves F and G.

These experiments seem to me to be in entire harmony with the view that the reducing action of so-called nascent hydrogen is connected with the existence of this body in the atomic state, and that any conditions tending to prolong the duration of this atomic condition augment the reducing power of the hydrogen. It is known from the observations of Berthelot, Cailletet, and others, that under very great pressures dilute sulphuric acid is without action on zinc, and the evolution of the hydrogen entirely ceases. It is not that the hydrogen is possibly liquefied, for the zinc is not dissolved. May it not be possible that the evolution of the hydrogen is connected with its existence in this atomic state? We assume that it comes from the hydrogen sulphate; enormous pressure may so alter its relations to the SO_4 molecule that the action of the zinc is insufficient to detach it.

The rapidity with which the hydrogen is evolved when the metal is placed in the acidulated solution of the ferric sulphate seems to depend on the position of the metal in the electro-chemical series. The more electro-positive the metal, the greater its rapidity of solution. The order in the electro-chemical series is—

Iron,
Zinc,
Magnesium.

The order of rapidity of solution is precisely the reverse—

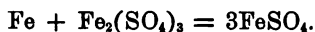
Magnesium,
Zinc,
Iron.

Any condition which increases the rapidity of the evolution of the hydrogen, without to an equal extent increasing the chance of contact of the hydrogen-atom with the ferric sulphate, diminishes the propor-

tion of hydrogen which does work as a reducing agent. By increasing the amount of free acid, we increase the rate at which the hydrogen is evolved, without to an equal degree increasing the molecular movement of the ferric sulphate, and hence an increased amount of hydrogen escapes. On the other hand, by keeping the amount of acid constant and heating the liquid, we increase the chances of contact between the ferric sulphate and hydrogen-atom, and accordingly obtain an increased reduction. By placing a given weight of zinc in contact with platinum, the actual amount of hydrogen which does work is not sensibly altered, although the quantity formed in a given time is increased.

By diluting the ferric sulphate solution the chances of contact between the hydrogen and ferric sulphate are of course diminished, and hence more of the hydrogen escapes in the free state. The effect of adding an indifferent salt, such as the zinc sulphate, to the solution, may be explained in the same way. It is now apparent why the reduction of the last traces of the ferric salt by the zinc, and more especially by the magnesium, is so tedious and difficult.

The experiments with iron seem at first sight at variance with one of these conclusions. Strictly speaking, however, they are not wholly comparable with the observations made with zinc and magnesium, owing to the tendency of the iron to act on the ferric sulphate to form ferrous sulphate or ferroso-ferric sulphate :



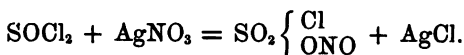
In this case the experiments ought to have been accompanied by determinations of the amount of hydrogen actually evolved, as the quantity retained cannot be fairly deduced from the amount of oxidisable iron present in the solution. The effect observed, therefore, is the resultant of two perfectly dissimilar reactions, the separate effects of which cannot be estimated.

These experiments are not without some value in reference to their bearing on the determination of iron by volumetric analysis. They serve to show why it is so tedious and difficult to effect the complete reduction of a ferric salt by the use of zinc, and *à fortiori* by that of magnesium. This fact, at least as regards zinc, has been already recognised by chemists in iron works, to whom the rapidity of a method is all important; many of these prefer to use such reducing agents as stannous chloride. There are, however, certain advantages attending the use of zinc, and accordingly this metal will continue to be employed by some. The foregoing observations serve to determine the conditions under which it can be most advantageously used.

XLV.—*Note on the Action of the Oxychlorides of Sulphur on Silver Nitrate.*

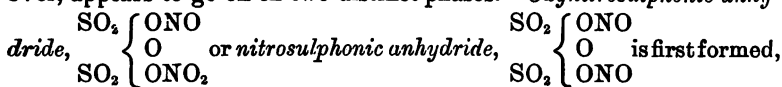
By T. E. THORPE, F.R.S.

THIONYL CHLORIDE, SOCl_2 , acts with great energy on silver nitrate with formation of *nitrosulphonic chloride* and silver chloride, apparently in strict accordance with the reaction—

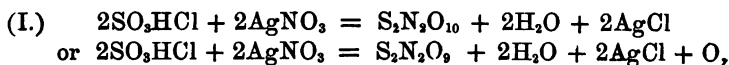


Sulphuryl chloride, SO_2Cl_2 , has no action on silver nitrate; the liquid may in fact be distilled off the salt with no perceptible decomposition.

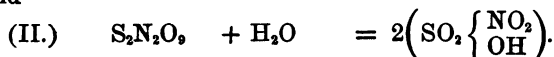
Chlorosulphonic acid, $\text{SO}_2\text{OH.Cl}$, also acts with great violence on silver nitrate, with formation, ultimately, of silver chloride and the so-called "chamber-crystals" or *nitrosulphonic acid*. The reaction, however, appears to go on in two distinct phases. *Oxynitrosulphonic anhydride*,



together with water: the two substances mutually reacting, with formation of nitrosulphonic acid and liberation of oxygen, thus:—



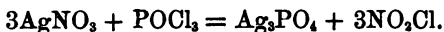
and



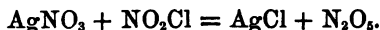
XLVI.—*On the Action of Thiophosphoryl Chloride upon Silver Nitrate.*

By T. E. THORPE, Ph.D., F.R.S., and SEPTIMUS DYSON, Esq.

ACCORDING to Odet and Vignon, nitroxyl chloride, NO_2Cl , may be readily obtained by acting upon silver nitrate with phosphoryl chloride:—



If excess of silver nitrate be present, the nitroxyl chloride reacts upon that salt with formation of silver chloride and nitrogen pentoxide, thus:—

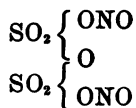


Odet and Vignon have indeed proved that in the method of making nitrogen pentoxide discovered by Deville, namely, by the action of chlorine upon silver nitrate, nitroxyl chloride is first formed, which afterwards reacts upon a second molecule of silver nitrate in accordance with the above equation.

The general analogy which exists between phosphoryl chloride and thiophosphoryl chloride has induced us to study the action of the latter compound upon silver nitrate in the hope that possibly a mixed anhydride might be formed; that is, a compound built up on the type of the pentoxide in which part of the oxygen was replaced by sulphur.

Preliminary experiments showed that thiophosphoryl chloride acts with great energy upon silver nitrate even in the cold, and that at least 3 and probably 4 molecules of silver nitrate are required for each molecule of the thiochloride. All the phosphorus was retained by the silver, together with a portion of the chlorine, whilst the whole of the sulphur was evolved.

64.47 grams of dry finely powdered silver nitrate were placed in a distilling flask connected with an inverted condenser, to the upper end of which was adapted a U-tube surrounded by a mixture of ice and salt; and 21.5 grams of recently distilled thiophosphoryl chloride were weighed out into a stoppered separating funnel fixed into the neck of the flask. Cork and caoutchouc were altogether avoided in making the joints, all the connections being formed either by fusion or by means of luting of gypsum subsequently dried at a high temperature. The thiochloride was allowed to fall drop by drop upon the nitrate; the reaction, which required no extraneous heat, was attended by the formation of a dense cloud of mixed red and white vapour, much of which was liquefied in the inverted condenser, and ran back into the flask. There was no difficulty in so regulating the action, that practically everything that would condense at the ordinary temperature was liquefied in the reflux condenser. In the U-tube placed in the freezing mixture at the extreme end of the apparatus was found a quantity of a limpid liquid of a dark green colour. On being removed from the freezing mixture it decomposed with great rapidity, and in the course of a few hours became solid. On replacing the tube in the freezing mixture comparatively little gas was evolved, but at the ordinary temperature a considerable amount was disengaged, and this was greatly increased on warming the tube with the hand. After a time the evolution of the gas ceased, and the solid residue became quite white. The gaseous products were found to be a mixture of nitrogen peroxide, nitric oxide and nitroxyl chloride: the solid residue was *nitrosulphonic anhydride*—;



as the following analyses show:—

- I. After having been heated to 75° 0.1995 gram gave 0.3859 gram BaSO₄.
- II. 0.4180 gram, after fusion, when no loss of weight was perceived, gave 0.8099 BaSO₄.

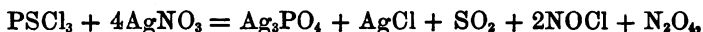
I.	II.	S ₂ N ₂ O ₅ requires
26.55	26.59	27.11

Nitrosulphonic anhydride boils at 360°: it is obvious therefore that it could not have existed pre-formed in the deep-green coloured highly volatile distillate which condensed in the freezing mixture: it must have been produced by the subsequent reaction or decomposition of the condensed products. Nitrosulphonic anhydride may indeed be formed by the action of sulphur on nitrogen pentoxide, and it is just possible that it is actually so produced in the flask by the action of the thiochloride upon the silver nitrate, but it is highly improbable that the anhydride found or formed in the distillate owes its origin to this reaction. It was most probably formed by the action of sulphur dioxide upon nitrogen peroxide, a reaction by which the body can be very readily obtained: the supposition that this was the mode of its origin is strengthened by the observation that sulphur dioxide was actually perceived in small quantity among the products escaping from the U-tube:

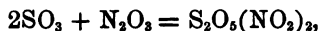


The occurrence of the trioxide accounts for the deep colour of the distillate and for the formation of the peroxide and dioxide among the gases which escape on removing the tube from the freezing mixture, since, as is well known, the trioxide is readily decomposed into these products at the ordinary temperature.

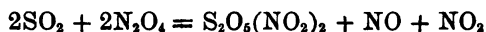
Thiophosphoryl chloride acts upon silver nitrate most probably therefore in accordance with the equation—



the condensed products afterwards reacting according to the equation—



or with greater probability according to that given above, viz.:—



We have no hope, therefore, of being able to form a mixed anhydride, on the type of nitric anhydride in which more or less of the oxygen is replaced by sulphur, by the substitution of thiophosphoryl chloride in Odet and Vignon's reaction.

XLVII.—Experiments on the Action of Potassium-amalgam, Sulphuretted Hydrogen, and Potassic Hydrate respectively, on Tetra- and Penta-thionate of Potassium.

By VIVIAN LEWES, Assistant in the Laboratories, Royal Naval College.

(1.) Action of Potassium-amalgam on a Solution of Potassic Tetrathionate.

SOME pure well-defined monoclinic crystals of anhydrous potassic tetrathionate, prepared by the process described by me in the *Chem. Soc. Journal*, 1881, 68, were dissolved in distilled water, and small pieces of potassium-amalgam added until the solution gave a slight alkaline reaction with litmus-paper.

No sulphur separated, and after the mercury and slight scum from the amalgam had been filtered off, the solution gave the following qualitative reactions.

- a. Argentic nitrate gave a white precipitate, darkening on warming.
- b. Baric chloride, slight white precipitate on standing, dense white precipitate on addition of alcohol, soluble in boiling water, and recrystallising on cooling.
- c. Hydric chloride on standing or warming gave a precipitate of sulphur, with evolution of sulphurous acid, but no sulphuretted hydrogen.
- d. Ferric chloride, deep violet colour, disappearing on standing.

From these reactions it is evident that the tetrathionate has been decomposed, with formation of thiosulphate.

The portion of the solution left after the foregoing experiments had been performed, was again tested with litmus-paper, and the faint alkaline reaction having disappeared, a small fragment of amalgam was added, the solution filtered, and excess of baric chloride and alcohol added; a dense white precipitate formed, which was filtered off, washed with cold water, and then boiled with excess of water,

which dissolved the whole of the precipitate, and on cooling deposited a crop of crystals.

These crystals were drawn, rinsed, dried, and analysed, giving results agreeing with the composition of baric thiosulphate.

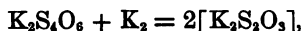
A saturated solution of potassic tetrathionate was then taken and potassium-amalgam added until it gave a faintly alkaline reaction. The clear liquid was decanted from the mercury and placed to crystallise over hydric sulphate in a vacuum, and yielded a crop of needle-shaped prismatic crystals, giving all the reactions of potassic thiosulphate.

A third solution of potassic tetrathionate was then taken, and potassium-amalgam added until the solution became strongly alkaline, the scum and mercury filtered off, and the clear solution tested, with the following results:—

- a. Argentic nitrate gave an immediate black precipitate ;
- b. Plumbic acetate, a black precipitate ;
- c. Hydric chloride, a precipitate of sulphur, with evolution of sulphurous acid and sulphuretted hydrogen ;

these reactions showing the presence of sulphide as well as thio-sulphate.

From the foregoing experiments it is evident that potassium amalgam added to a solution of potassic tetrathionate causes a decomposition of the tetrathionate with formation of thiosulphate—



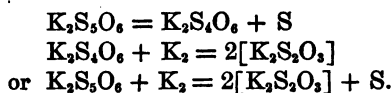
and that the addition of more potassium than is required for this decomposition causes the formation of sulphide.

(2.) *Action of Potassium-amalgam on Potassic Pentathionate.*

Some fine crystals of potassic pentathionate were dissolved in water, and potassium-amalgam was added piece by piece to the solution, causing at once a considerable precipitate of sulphur. As soon as the liquid became slightly alkaline, the sulphur was filtered off, but on standing, the clear solution again became opalescent; it was again filtered, and the solution remained clear, and behaved in all respects like the potassic thiosulphate formed by the reduction of the tetrathionate.

A further addition of potassium-amalgam to this solution caused the formation of sulphides.

Hence it is evident that the pentathionate is first reduced to tetrathionate with separation of sulphur, and that the tetrathionate is then converted into thiosulphate.



(3.) *Action of Sulphuretted Hydrogen on Potassic Tetrathionate.*

Five grams of potassic tetrathionate were taken, dissolved in water, and well washed, and hydric sulphide passed through the solution until it became saturated; it was then allowed to stand in a well stoppered bottle for several hours, at the end of which all smell of hydric sulphide had disappeared, and a considerable deposit of sulphur had taken place.

The solution was again saturated with the gas, and again, on standing, all smell disappeared; at last, after several saturations, the smell of hydric sulphide became constant, even after standing a week, and the solution was then filtered through a paper, the weight of which was known, and the clear filtrate placed in a dish, over lumps of potassic hydrate in a desiccator, to free it from all undecomposed hydric sulphide. The solution was then evaporated to dryness in a vacuum, and deposited a crop of prismatic needles, round the base of which an amorphous salt was deposited. This amorphous salt on recrystallisation yielded prismatic needles of the same form as the previous ones.

The sulphur deposited on the tared filter was weighed, after having been well washed and dried, and the weight of salt formed by the decomposition was also ascertained.

Sulphur deposited = 2.604 grams
Salt formed = 3.1 „

The salt formed was then analysed qualitatively, with the following results:—

- a. Argentic nitrate gave with an aqueous solution of the salt, a white precipitate, darkening on warming.
- b. Hydric chloride gave on standing a precipitate of sulphur, with evolution of sulphurous acid gas.
- c. Ferric chloride gave a deep violet coloration.
- d. Baric chloride gave a white precipitate, soluble in excess of hot water, and recrystallising on cooling.

The remainder of the salt was then analysed quantitatively, the sulphur being determined by oxidation with fuming nitric acid, and weighed as baric sulphate after due precautions had been taken to free it from baric nitrate.

The potassium was estimated as potassic sulphate—

Potassium = 35.8 per cent.
Sulphur = 33.2 „

which nearly agrees with the calculated composition of Kessler's potassic hyposulphite ($3[\text{K}_2\text{S}_2\text{O}_3]\text{H}_2\text{O}$).

From these results it appears that sulphuretted hydrogen, when passed into a solution of potassic tetrathionate, reduces it to potassic thiosulphate with precipitation of sulphur.



and this reaction probably takes place in two stages—

1. $\text{K}_2\text{S}_4\text{O}_6 + \text{H}_2\text{S} = \text{K}_2\text{S}_2\text{O}_3 + \text{H}_2\text{S}_2\text{O}_3 + \text{S}$
2. $\text{H}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{S} = 3\text{H}_2\text{O} + \text{S}_4$.

If we now take this equation and calculate from it the amount of sulphur deposited and potassic thiosulphate produced by the decomposition of 5 grams of potassic tetrathionate, we obtain numbers agreeing very closely with those found in the foregoing experiments:—

	Calculated.	Found.
Salt taken	5.0 grams	5.0
Sulphur deposited ..	3.14 „	3.1
Hyposulphite formed	2.64 „	2.634

In order to make sure that the sulphur deposited did not contain any salt, it was ignited—

$$\begin{array}{rcl} \text{Crucible} + \text{ash} & = & 15.87 \\ \text{Crucible} & = & 15.868 \\ \hline \text{Ash} & = & 0.002 \end{array}$$

and as the ash of the filter used would weigh 0.0015 gram, the sulphur was practically pure.

(4.) *Action of Potassic Hydrate upon a Solution of Potassic Pentathionate.*

If potassic hydrate be added in excess to a solution of Wackenroder pentathionic acid, the higher thionates are entirely decomposed with formation of thiosulphate, sulphite, and precipitation of sulphur—



This can easily be proved qualitatively, as has been done by Messrs. Takamatsu and Smith (*Chem. Soc. J., Trans.*, 1880, 592), but no quantitative proof of the correctness of the equation is possible, owing to the uncertain composition of the Wackenroder acid.

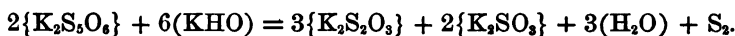
Some pure crystals of potassic pentathionate were taken, weighed, and dissolved in a few drops of water, and 5 c.c. of a potassic hydrate

solution of known strength added. This produced an immediate precipitate of sulphur, which was made to coagulate by shaking, and was then filtered off, the filtrate and wash-water being titrated with standard acid, to determine the amount of potassic hydrate used up in the decomposition of the salt.

Weight of potassic pentathionate taken was 0.914 gram, which required for its decomposition 0.4318 gram of potassic hydrate, and if these numbers are divided by the molecular weight of the compounds to which they refer—

$$\frac{0.914}{0.334} = 0.0027; \quad \frac{0.4318}{56} = 0.0077.$$

quotients are obtained which stand to one another nearly in the ratio of 1 to 3, pointing to the equation—



(5.) *Action of Potassic Hydrate upon a Solution of Potassic Tetrathionate.*

Pure crystals of potassic tetrathionate were taken, dissolved in water, and known quantities were mixed with potassic hydrate in solution in the ratios—

(1.)	2	molecules	$K_2S_4O_6$	to	4	molecules	KHO
(2.)	3	"	"		8	"	"
(3.)	4	"	"		12	"	"

These mixtures were sealed up in tubes, and allowed to stand for some days, and were then opened, and after being made up to a known volume with distilled water, were carefully examined, the object being to ascertain if sulphates were formed when potassic hydrate acts upon the tetrathionate in any of the above proportions.

In no case was any trace of sulphate found, the reactions seeming to be always productive of thiosulphate and sulphite.

The presence of these products of decomposition was proved in the case of tube (3), by precipitating them with baric chloride, and boiling the precipitate for some time with excess of water, filtering hot, and washing the precipitate with boiling water.

The precipitate was then dried and weighed, the filtrate and wash-water being concentrated and placed to crystallise.

The potassic tetrathionate taken in this experiment weighed 2.94 grams, and yielded 2.3 grams of baric sulphite, equivalent to 1.7 grams of potassic sulphite.

This baric sulphite was entirely soluble in hydric chloride, but after

standing the acid solution became slightly opalescent, showing that a small quantity of thiosulphate had remained in the sulphite.

If these numbers be divided by the molecular weights of potassic tetrathionate and sulphite respectively, we obtain quotients standing to each other nearly in the ratio of 1 to 1, the slight discrepancy being due to the trace of thiosulphate remaining undissolved.

The filtrate and wash-water from the baric sulphite on standing deposited a fine crop of small rectangular prismatic crystals, which were drawn, and dried over hydric sulphate, weighed, and analysed quantitatively, giving—

Barium = 50·8 per cent.

Sulphur = 23·3 ,,

agreeing with the composition of baric thiosulphate, with 1 mol. of water of crystallisation.

2·435 grams of potassic tetrathionate were then dissolved in a little water, and were sealed up in a glass tube with a known quantity of potassic hydrate, and allowed to stand in a warm place for two days. No separation of sulphur took place. The tube was then opened, and the amount of potassic hydrate remaining uncombined determined by rapid titration with a solution of standard acid.

It was found that 1·3288 grams of potassic hydrate had been required for the decomposition of the 2·435 grams of potassic tetrathionate, and dividing these numbers by 302 and 56 respectively, we obtain the quotients 0·008 and 0·0024, which stand to each other as 1 to 3.

From these experiments it is evident that when potassic hydrate acts upon potassic tetrathionate, potassic sulphite and thiosulphate are formed; also that for every molecule of the tetrathionate, 3 molecules of potassic hydrate are required, and 1 molecule of potassic sulphite is formed, results which conclusively point to the equation—



I have been for some time at work upon other reactions of the higher thionates, and hope shortly to place the results before this Society.

XLVIII.—On the Estimation of Retrograde Phosphates.

By FREDERICK JAMES LLOYD.

It has long been known that in some superphosphates the percentage of phosphate, soluble in water, gradually decreases. The phosphate which has become insoluble is termed "retrograde phosphate." The cause of this change has attracted considerable attention, both from the manure manufacturer and the chemist. The manufacturer discovered that it was brought about in poorly-made superphosphates, and also in those made from phosphates containing iron and alumina. It has subsequently been said that magnesia and lime are both capable of producing this change. Many attempts have been made to show the exact composition of retrograde phosphates, but with no satisfactory results. There is a question, however, which has a wide agricultural and commercial interest, and to which I shall attempt to give some answer. Can retrograde phosphates be estimated?

The first attempt to estimate them was made by J. A. Chesshire (*Chem. News*, 19, 229) in 1869, by dissolving them in ammonium oxalate. John Hughes (*ibid.*, 19, 266) at once showed the fallacy of this method, for that ammonium oxalate acted upon coprolites and phosphatic minerals, the raw materials from which superphosphates are manufactured. Subsequently, Chesshire (*ibid.*, 20, 111) proposed sodium bicarbonate as a solvent, with, however, no better result.

In 1871, Fresenius, Neubauer, and Luck (*Fresenius' Zeitschrift*, 10, 133) examined the various methods which had then been proposed for the estimation of retrograde phosphates, and found them all faulty. At the same time they suggested that a neutral solution of ammonium citrate of sp. gr. 1.09 should be used as a solvent, and they laid special stress on its being neutral. As in the following references the percentage of citric acid used is given, it may be at once stated that a solution of ammonium citrate of sp. gr. 1.09 contains 18.5 per cent. citric acid.

In 1873, Joulie (*Moniteur Scientifique* [3], 2, 213) suggested an ammonium citrate solution containing 40 per cent. of citric acid, not merely neutralised by ammonia, but made strongly alkaline with a large excess of ammonia. He claims for his method that it was not based upon nor suggested by Fresenius' paper. Luck (*Fresenius' Zeitschrift*, 14, 313) disputes this statement, and also says that it is not material whether the ammonium citrate solution be neutral or strongly ammoniacal.

Dr. A. Petermann (*Ann. Agronomiques*, 1880) at first adopted the

neutral solution proposed by Fresenius. In 1879, however, he points out the necessity of making the solution ammoniacal, and adds to the litre of solution 50 c.c. of ammonia.

Of the very many articles written upon the subject of retrograde phosphates, these appear to me the most important which bear upon their estimation. Nevertheless, many analytical chemists consider that there is still no accurate method of determining them.

My first experiments were directed to find out the relative dissolving power of citric acid upon phosphates and other substances likely to be present in superphosphates and manures, when the citric acid was partly neutralised, wholly neutralised, and more than neutralised by ammonia. Three solutions were made. One contained 20 per cent. of citric acid, together with enough ammonia to have neutralised 25 per cent. of citric acid. The second solution contained 20 per cent. citric acid, neutralised. The third solution was acid, only 15 parts of the citric acid being neutralised, and 5 parts being free acid. After having made some experiments, I noticed what stress Fresenius laid upon the necessity of the solution being absolutely neutral. Upon testing the neutralised solution, it was found to be very slightly acid. This is due to the difficulty of distinguishing between a nearly and absolutely neutral solution of ammonium citrate, as neither litmus, phenol-phthalein, nor methyl-orange can be used as indicator. The litmus-paper requires to be left in the solution for a day or two. Another neutral solution containing 20 per cent. citric acid was made, and turned very slightly alkaline, there being, however, only a few c.c. of ammonia in excess in a litre.

In my experiments either 1 or 2 grams of the substance were taken, most intimately triturated with 50 c.c. of citrate solution in a mortar, washed into a measure-glass, and made up to 100 c.c. with distilled water, shaken up several times, and allowed to stand all night. Next morning the supernatant liquid was filtered, until over 50 c.c. had come through quite clear. Of this filtrate, 50 c.c. were taken for analysis. The lime was taken out by ammonium oxalate, after neutralising with ammonia and acidifying with acetic acid, as usual, and the phosphoric acid by magnesium mixture from the filtrate. The magnesium phosphate precipitate was redissolved and reprecipitated in all cases. A similar quantity of each substance was treated with distilled water, and in all respects in exactly the same manner as if with a citrate solution. All the experiments were done at the ordinary temperature of the laboratory, so that the solutions, while in contact with the substance, never exceeded a temperature of 16° C. In order not to complicate the results, no allowance has been made for the phosphoric acid which remains soluble in the ammonium citrate solution, when estimated by magnesia. The results are given in the table

on p. 309; the figures represent the quantity of substance dissolved out of 100 parts of the substance acted upon.

The most striking point in these results is the vast difference between the solvent power of a very slightly alkaline solution as compared with a slightly acid solution. It deserves attention, as it bears materially upon Fresenius' method of estimating retrograde phosphates. Next it will be noticed that while an ammoniacal solution is less able to dissolve coprolites, bone-ash, and bone-meal than a neutral solution, it has quite the reverse effect upon precipitated phosphates, and is more powerful as a solvent. Luck, therefore, is mistaken in saying that the addition of ammonia to Fresenius' solution has no effect.

It is evident that no satisfactory determination of retrograde phosphates can be made by an acid, or even a slightly acid solution of ammonium citrate, owing to the powerful action which they exert upon other substances.

The next experiments were directed to discover the effect of ammoniacal solutions of ammonium citrate; whether the proportion of citric acid present was of much importance, and whether the proportion of ammonia in excess had any influence on the results.

For this purpose six solutions were made, two containing 20 per cent. citric acid, two 30 per cent. citric acid, and two 40 per cent. citric acid. One of each pair of solutions contained ammonia in excess sufficient to neutralise one-fourth more citric acid than was present; the other sufficient ammonia in excess to neutralise one-half more citric acid than was present. These experiments were also made in the cold, and in all respects in a similar manner to the former ones. The results are given in the table (p. 309).

The conclusion which may justly be drawn from these results is that an ammoniacal solution of ammonium citrate, no matter what may be its strength, whilst capable of dissolving precipitated phosphate of lime, does not act either upon mineral phosphates, or upon bone-ash, and only to a very slight extent upon raw bones.

I found considerable difficulty in taking out the lime with oxalate of ammonia in some of my experiments. Oxalate of lime appears to be soluble in a concentrated solution of ammonium citrate, such as the 40 per cent. solution. This I believe to be the explanation of no lime being found in some of the experiments on bone-meal, rather than that no lime was dissolved by the ammonium citrate solutions.

The power of ammonium citrate to hold lime in solution is well known, and Petermann considers it possible to precipitate phosphoric acid with magnesia mixture, without first taking out the lime, provided a sufficient quantity of ammonium citrate be present. A large number of experiments have convinced me that this method is

Solvent.	Substances.									
	Ground Cambridge Coprolites.		Bone-ash.		Bone-meal.		Precipitated* Phosphate A.		Precipitated* Phosphate B.	
	CaO.	P ₂ O ₅ .	CaO.	P ₂ O ₅ .	CaO.	P ₂ O ₅ .	CaO.	P ₂ O ₅ .	CaO.	P ₂ O ₅ .
Water.....	0.11	—	0.05	0.06	0.22	0.25	2.35	1.15	3.41	1.02
Citrate of ammonium:—										
Cit. acid 20 per cent., ammoniacal.....	—	—	—	—	2.52	1.85	12.09	12.54	12.43	9.72
" " " slightly ditto	0.11	—	0.61	0.64	6.55	4.80	8.51	8.83	8.01	6.20
" " " acid	2.57	0.89	2.29	1.40	12.09	8.96	21.61	22.01	28.11	22.52
" " " acid	3.92	1.47	8.51	6.40	17.52	13.18	22.28	23.55	29.23	23.80
" " "	—	—	—	—	0.67	1.28	—	—	12.43	9.85
" " " $\frac{1}{2}$ ammonia in excess	—	—	—	—	0.67	1.28	—	—	13.10	10.36
" " " $\frac{1}{4}$ " " "	—	—	—	—	1.23	1.34	—	—	13.44	10.49
" " " 30 per cent., $\frac{1}{4}$ " " "	—	—	—	—	—	1.21	—	—	12.20	11.13
" " " " " " $\frac{1}{4}$ " " "	—	—	—	—	1.12	1.21	—	—	12.76	11.39
" " " 40 per cent., $\frac{1}{4}$ " " "	—	—	—	—	—	0.70	—	—	11.87	10.62
" " " " " " $\frac{1}{4}$ " " "	—	—	—	—	—	0.64	—	—		

* For the composition of these phosphates see *post*.

erroneous, and that no matter what proportion of ammonium citrate be present, accurate results cannot be obtained except by accident. Herzfeld and Feuerlein (*Fresenius' Zeitschrift*, 14, 185) have shown that the precipitate of ammonium magnesium phosphate obtained in this manner invariably contains more or less lime.

To decide whether the ammoniacal solutions would act upon retrograde phosphates when present in superphosphates, it was necessary to obtain superphosphates containing them. None of the high-class superphosphates having about 35 per cent. of soluble phosphate appear to undergo this retrograde change. For instance, in March of last year the soluble phosphoric acid in two superphosphates was 15.84 per cent. and 16.29 per cent. respectively; in January this year these superphosphates contained 15.80 per cent. and 16.16 per cent. The retrogression takes place chiefly in superphosphates which contain a large quantity of insoluble phosphates.

A superphosphate, No. 289, having, in March, 1881, 4.24 per cent. of phosphoric acid, soluble in water, contained in January, 1882, only 2.42 per cent., thus showing that 1.82 per cent. of phosphoric acid had passed into retrograde phosphates.

After several trials it appeared to me better to determine the retrograde phosphates, together with the soluble phosphate, in a separate portion of superphosphate rather than in the residue of that portion from which the soluble had been washed out.

The effect of the six ammoniacal solutions upon this superphosphate was tried. In no case was the total quantity of retrograde phosphoric acid found. The strongly ammoniacal 30 per cent. solution of citric acid, however, gave the best results.

I tried whether the addition of ammonium chloride would increase its solvent power, but the results showed it had no effect whatever.

I next compared the action of this strongly ammoniacal solution of 30 per cent. citric acid with the solutions proposed by others: 1st, that by Fresenius, viz., a neutral solution of sp. gr. 1.09; 2nd, that of Petermann, which is the same solution with 50 c.c. ammonia per litre added; and 3rd, that of Joulie, which is the 40 per cent. strongly ammoniacal solution. But in order more accurately to compare the relative effect of these solutions, 2 grams of superphosphate and 50 c.c. of solution were taken in each case, made up to 100 c.c. with water, and 50 c.c. taken for analysis. These experiments were made in the cold.

The results were as follows:—

	Superphosphates.		
	No. 289.	No. 319.	No. 337.
Soluble P_2O_5 in 1881	4.24	10.77	11.06
Soluble P_2O_5 in 1882	2.42	9.92	10.36
Phosphoric acid present as retrograde phosphates ..	1.82	0.85	0.70
Total phosphoric acid found with—			
Fresenius' solution	3.13	9.41	9.79
Petermann's solution	3.26	5.57	5.25
Strongly ammoniacal 30 per cent. solution.....	3.58	8.96	9.02
Joulié's solution	3.77	8.70	9.21

These results confirm the close relation between the power of the strongly ammoniacal 30 per cent. and 40 per cent. citric acid solutions. In neither case was the total phosphoric acid found, whilst in two sets of the experiments not even the whole of the soluble phosphoric acid was obtained in solution. It appeared evident, therefore, either that the quantity of superphosphate operated upon, viz., 2 grams, was too large, or that the solutions had not been sufficiently diluted.

By following closely the directions given by the author of each process, these points would be tested.

No further experiments were made with Fresenius' solution, for as he recommends 2 grams to be taken, it appeared evident from its action on superphosphates No. 319 and No. 337 that it was not capable of yielding accurate results without the application of heat. Although it had given high results, this appeared due to the solution being turned acid when it came in contact with the superphosphate. This supposition is not confirmed by experiment. For instance, 2 grams of the superphosphate No. 337 were treated first with dilute ammonia until alkaline, and then with Fresenius' solution; 9.66 per cent. of phosphoric acid were obtained, which corresponds closely with that given by the acid superphosphate. I cannot explain this result, but hope to take up the subject in some future experiments.

The methods adopted in testing the processes, as given by their authors, were as follows:—

With Petermann's solution: 2 grams of superphosphates were treated with 100 c.c. of solution, made up to 500 c.c. with water, and 100 c.c. taken for analysis. No heat however was applied, as he directs.

With Joulié's solution: 1 gram of superphosphate was treated with 50 c.c. of solution, made up to 100 c.c., and 50 c.c. taken for analysis.

With the strongly ammoniacal 30 per cent. solution in one experiment 1 gram was treated with 50 c.c. of solution, made up to 100 c.c. with water, and 50 c.c. taken for analysis.

In the other experiment 2 grams were treated with 50 c.c. of solution, made up to 200 c.c. with water, and 100 c.c. taken for analysis.

The following are the results obtained:—

	No. 319.	No. 337.		
Phosphoric acid soluble in 1881	10.77	11.06		
" " " 1882	9.92	10.36		
	<hr/> 0.85	<hr/> 0.70		
Phosphoric acid found—				
	Total.	Retrograde.	Total.	Retrograde.
By Petermann's method ..	9.60	—	10.40	0.04
30 per cent. solution on				
1 gram	10.88	0.96	11.77	1.41
30 per cent. solution on				
2 grams	9.28	—	10.17	—
Joulie's solution	10.75	0.83	11.77	1.41

The superphosphate No. 337 appears to have originally contained some retrograde phosphate. The chief conclusions which may be drawn from these and previous results, are that the extent of dilution with water does not affect the results to a sufficient extent to make them accurate; that Petermann's method is not trustworthy without the application of heat; and that the 30 per cent. and 40 per cent. solutions are almost exactly similar in their action, and do yield accurate results under certain conditions.

Before endeavouring to ascertain these conditions, I may state my reason for discarding the methods of Fresenius and Petermann is that they both heat their solutions to a temperature of 35° C. I believe I have shown that they cannot obtain accurate results without the application of heat. If the solutions are to be raised only to a certain temperature and no further, time and care must be bestowed upon each operation, and the method is of necessity inferior to one which can be carried out in the cold. To raise the solution to the temperature of boiling water would be easy. I therefore tried experiments with the various solutions on superphosphates to see what effect this heat had. Fresenius' neutral solution became acid, Petermann's solution became turbid, and could not be filtered. The 30 per cent. and 40 per cent. strongly ammoniacal solutions remained alkaline. The experiments were made on superphosphate No. 289 which originally contained 4.24 per cent. of phosphoric acid. The quantities found after boiling were:—

	Per cent. P_2O_5 .
With Fresenius' solution	5.69
„ 30 per cent. solution	5.18
„ Joulie's solution	5.50

in all cases far more than had ever been soluble. That the increased solvent power of the solution is due entirely to its increased temperature, was shown with a 40 per cent. ammoniacal solution upon precipitated phosphate B. This solution dissolved—

	CaO.	P_2O_5 .
In the cold.....	11.87	10.62
Boiled for one minute.....	12.54	14.08

The impracticability of heating the solution just to the temperature at which it gives accurate results is self evident.

The conditions under which accurate results might be obtained in the cold with the 30 per cent. and 40 per cent. solutions, and to decide which was the better, now remained to be settled.

The striking difference in the results, due to the quantity of substance operated upon, is best seen by the following table:—

	Super. 319.		Super. 337.		Super. 289.	
	1 gram.	2 grams.	1 gram.	2 grams.	2 grams.	4 grams.
Fresenius' solution.....	—	—	—	—	2.94	2.72
30 per cent. solution....	10.88	8.96	11.77	9.02	3.58	2.56
Joulie's solution.....	10.75	8.70	11.77	9.21	3.77	3.10

It was consequently necessary to discover the greatest quantity of soluble phosphate which the 50 c.c. of 30 per cent. or 40 per cent. solution was capable of dissolving from 1 gram of superphosphate. Operating upon a high class superphosphate containing 16.29 per cent. of phosphoric acid soluble in water, the following results were obtained:—

	CaO.	P_2O_5 .
30 per cent. solution	20.16	14.08
40 „ „ (Joulie)	15.23	14.20

The presence of iron and alumina, however, considerably decreases the solvent power of the ammonium citrate solution, so that the maximum quantity which could be dissolved from a superphosphate, to which these had been added, was in four separate determinations 11.90 per cent. of phosphoric acid, although 13.30 per cent. of soluble phosphoric acid was present.

The smaller the quantity of superphosphate taken for analysis the more accurate are the results, and any error will consist, not in finding more retrograde phosphate than actually exists, but in not finding all that is present.

My experience shows that 0.5 gram is enough to take with very high class superphosphates. The multiplication of any error which takes place when using so small a quantity is considerable. I believe larger quantities might be operated upon if the superphosphate is first treated once with cold water to dissolve out the main portion of the soluble phosphate.

To confirm the satisfactory results which had been obtained with the 30 per cent. solution acting upon 1 gram, two more experiments were made. The following are the results:—

	No. 289.	No. 309.
Soluble phosphoric acid in 1881 ..	4.24	11.04
" " in 1882 ..	2.42	10.56
Retrograde	1.82	0.48
Total phosphoric acid found with		
30 per cent. solution	4.35	11.01

To test the possibility of the solution dissolving bones, if present in a superphosphate, its effect was tried upon a manure which had recently been made, by mixing superphosphate with bones. There was 20 per cent. of bones present in the manure, and 7.64 per cent. of soluble phosphoric acid. Treated with 30 per cent. solution, the total phosphoric acid soluble was 7.68 per cent. The bones were not acted upon.

The effect of the solution was next tried upon dissolved bones. These had been first analysed in 1881, but how soon after their manufacture was not known. The results obtained were as follow:—

	No. 192.	No. 248.
Soluble phosphoric acid in 1881....	7.79	9.17
" " in 1882....	7.80	9.18
Soluble in 30 per cent. solution	9.21	10.36

As the experiment on the mixed manure, as well as the early experiments with the six ammoniacal solutions, show that the 30 per cent. solution has very little action upon raw bones, the only explanation which I can give of these results is, that dissolved bones contain some phosphate, the result of a partial action of the sulphuric acid on the bones, which phosphate, though not soluble in water, is soluble in ammoniacal ammonium citrate solution.

It has been stated by Millot (*Ann. Agronomiques*, 1880) that

Joulie's solution does not dissolve some kinds of *precipitated* phosphates. As this argument would necessarily apply to the 30 per cent. solution, I would point out that the object in view is to estimate *retrograde* phosphates. The phosphate which Millot refers to was made by adding carbonate of lime to a superphosphate. What proof is there of such a phosphate ever being formed naturally in a superphosphate? It is conceivable that by acting upon a superphosphate after it is made, phosphates may be formed not soluble in ammoniacal citrate of ammonia solutions. But before this can be used as an argument against the estimation of retrograde phosphates, it must be shown that such phosphates exist in superphosphates.

In the artificial production of precipitated phosphates, either of two reactions may take place. The substance added might be acted upon by the acid superphosphate, and a new compound formed, which takes place if carbonates are added to superphosphates. Or the substance, if unacted upon and soluble in water might, upon the addition of water, produce a precipitate with the portion of the superphosphate soluble in water, and so, apparently, give rise to the presence of retrograde phosphate where, in reality, there was none.

Some experiments were made by adding to a superphosphate 10 per cent. of (i) calcium chloride; (ii) ferrous sulphate; (iii) aluminic sulphate; (iv) magnesium sulphate. With the exception of calcium, I chose sulphates as being the salts most probably present in superphosphates. The original superphosphate contained 14.75 per cent. soluble phosphoric acid. Making allowance for the increase of weight due to the addition of the salts, the mixtures ought to contain 13.41 per cent. of soluble phosphoric acid.

The action of the 30 per cent. and 40 per cent. strongly ammoniacal ammonium citrate solutions was tried in each experiment, 0.5 gram of superphosphate being taken.

The results were—

	I. Calcium.	II. Iron.	III. Alumina.	IV. Magnesia.
Soluble phosphoric acid. . .	13.28	11.58	13.47	13.21
Total phosphoric acid found				
with 30 per cent. solution	13.31	13.31	13.31	9.47
Total phosphoric acid found				
with 40 per cent. solution	13.31	13.44	13.05	10.24

These experiments show an important point, confirmed by other experiments, that salts of magnesia are the only soluble salts likely to be present in a superphosphate which interfere with the method of estimating retrograde phosphate here proposed.

I have endeavoured to find out the composition of some of the phosphates dissolved by ammonium citrate solutions.

Bone Phosphate.—If we take the phosphoric acid and lime, dissolved from bone-meal by the various solutions, we find they are not in the same proportions as they are in tricalcic phosphate, the lime being in excess of the necessary quantity. The composition of the substance dissolved appears to be $\text{Ca}_{10}(\text{CO}_3)_6(\text{PO}_4)_3$, which is given by Hoppe-Seyler as the composition of the phosphate of bones, and is now generally accepted as such by modern physiologists.

The following figures will, I think, bear out this supposition:—

P_2O_5 found.	CaO found.	CaO calculated.
1·85	2·52	2·43
4·80	6·55	6·30
8·96	12·09	11·77
13·18	17·52	17·32

This phosphate is only sparingly soluble in ammoniacal ammonium citrate solutions.

Precipitated Calcium Phosphate.—The composition of the phosphates present in commercial precipitated phosphate depends *inter alia* upon the proportion of lime used in its manufacture.

The composition of the precipitated phosphates used in these experiments was—

	A.	B.
Moisture	28·75	19·90
Water of combination, &c. ..	8·25	9·01
Phosphoric acid	31·44	28·68
Lime	29·80	33·93
Alkaline salts, &c.	1·76	6·88
Silica	traces	1·60
	<hr/> 100·00	<hr/> 100·00

The precipitated phosphate soluble in A appears to have the composition $\text{Ca}_3\text{P}_2\text{O}_8, \text{Ca}_2\text{H}_2\text{P}_2\text{O}_8$. Millot has found a similar phosphate in some superphosphates.

The following are the figures found, compared with those necessary by calculation:—

P_2O_5 found.	CaO found.	CaO calculated.
12·54	12·09	12·36
8·83	8·51	8·71
22·01	21·61	21·84
23·55	22·28	23·22

The phosphate dissolved out of B appears to have the composition of ordinary tricalcic phosphate, $\text{Ca}_3\text{P}_2\text{O}_8$, as shown by the following figures:—

P ₂ O ₅ found.	CaO found.	CaO calculated.
9.72	12.43	11.50
6.20	8.00	7.33
22.52	28.11	26.64
23.80	29.23	28.15

This shows how soluble precipitated tricalcic phosphate is as compared with mineral tricalcic phosphate.

I trust these experiments have proved the possibility and conditions of the accurate estimation of retrograde phosphates.

XLIX.—*Action of Heat on Mercuric Chloride under Low Pressures.*

By THOS. CARNELLEY, D.Sc., Professor of Chemistry in Firth College, Sheffield.

A LITTLE more than a year ago I exhibited to the Society some experiments on the action of heat on ice and mercuric chloride under low pressures, and subsequently read a paper on the same subject before the Royal Society (*Proc. Roy. Soc.*, 209, 1881), in which I advanced two propositions—(1.) That when the superincumbent pressure is maintained below a certain point, called the critical pressure, it is impossible to melt ice, mercuric chloride, and probably other bodies, no matter how great the heat applied. (2.) That under these circumstances ice and mercuric chloride attain temperatures considerably above their natural melting points without fusion. Since the publication of the paper referred to, a number of chemists and physicists have repeated my experiments, and have all verified my first proposition; but, on the other hand, have been unable to observe any rise in temperature of the ice and mercuric chloride above their ordinary melting points under the circumstances indicated. Early last year, therefore, I determined to go over my experiments again with the very greatest care, and for this purpose I commenced with mercuric chloride, as the manipulation in this case is very much more simple than in that required for ice. The work has taken much longer than I expected, chiefly owing to an anomalous result obtained in the calorimetrical experiments which I have made. In this paper I shall describe the results I have obtained with mercuric chloride, leaving the discussion of the ice, with which I am at present engaged, to a future communication.

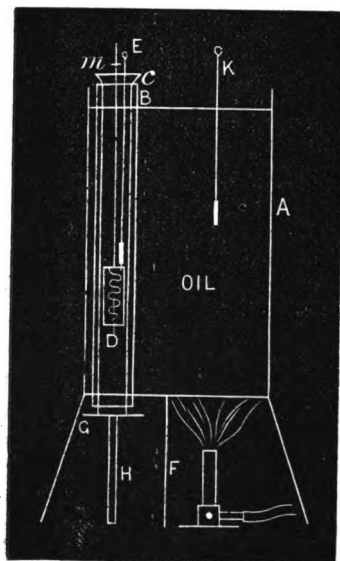
The temperature of the mercuric chloride was determined—(a.) Thermometrically; (b.) Calorimetrically.

(a.) *By the Thermometer.*—The results showed that when the mercuric chloride is in the form of a compact powder, the temperature rises 21° , and sometimes as much as 50° and more, above the melting point ($277^{\circ}\text{C. corr.}$) of the mercuric chloride without fusion. When the salt is in the form of a resolidified cylinder, the temperature rises to 15° above the melting point, the bulb and lower portion of the stem being in all cases completely covered by the salt, and the thread remaining intact.

(b.) *By the Calorimeter.*—For the determination of the temperature of the mercuric chloride, it was necessary to find the specific heat of the solid salt between its melting point and the ordinary temperature of the air. The method employed for this purpose was as follows:—

The salt was fused in a (6-inch \times $\frac{5}{8}$ -inch) test-tube, so that the latter was about two-thirds full, and a weighed platinum spiral was suspended in the mercuric chloride by a piece of fine platinum wire. The salt was then allowed to solidify, the test-tube removed, and the cylinder of mercuric chloride D, Fig. 1, suspended in the axis of the glass tube C ($\frac{7}{8}$ -inch diam.), which fits through the iron tube B of the linseed oil-bath A. The tube B passes down one side of the oil-bath and out at the bottom; both B and C are open at the lower extremity. The end of C, which is ground, projects a little beyond the bottom of the oil-bath, and is closed by a ground-glass plate G. The upper end of C is closed by a cork, through which a thermometer E passes, the lower

FIG. 1.



end of the bulb of which rests on the cylinder of mercuric chloride. The thermometer is so arranged that, the whole of the mercurial column being in the tube C, no correction will be required. A suspended plate of iron F is rivetted on to the bottom of the bath to protect the bottom of the tube C and the calorimeter from the direct heat of the lamp. The thermometer K serves to indicate the temperature of the bath, which is heated to the requisite point by means of a large Bunsen lamp, before the mercuric chloride is suspended in the tube C. The mercuric chloride is allowed to remain in the bath for at least three-quarters of an hour, when the temperature of E is read off, the plate G removed, and the calorimeter, the temperature of which has been previously observed, is brought under the mouth of the tube C. The suspending wire is then cut at *m*, when the salt drops into the calorimeter, which is at once removed, and the contained turpentine well stirred by agitating the mercuric chloride by means of the suspending wire, and the highest temperature attained read off.

The results obtained by using different liquids in the calorimeter are represented below, along with those obtained by Kopp and Regnault respectively.

Specific Heat of Mercuric Chloride.

Carnelley.			Kopp.	Regnault.
In petroleum.	In turpentine.		In coal-tar naphtha.	In turpentine.
	1st series.	2nd series.		
0·0644 at 240°	0·0709 at 230°	0·0673 at 152°	0·0636 at 45°	0·06954 at 98°
0·0643 at 244	0·0675 at 240	0·0676 at 168	0·0657 at 44	0·06821 at 98
0·0641 at 247	0·0696 at 250	0·0672 at 191	0·0628 at 46	
0·0642 at 248	0·0680 at 266	0·0676 at 209		
0·0632 at 253		0·0696 at 241		
		0·0670 at 253		
0·06404	0·06898	0·06771	0·0640	0·06889

This table shows conclusively that a much higher result (about 0·069) is obtained when turpentine is used than when petroleum is employed (viz., about 0·064), and also that Kopp, who used coal-tar naphtha, obtained a much lower number (0·064) than Regnault (0·069), who used turpentine, and further, that Kopp's result is almost identical with that obtained by myself with petroleum; whilst Regnault's is almost identical with that I obtained with turpentine.*

* Regnault (*Pogg. Ann.*, 53, 78) obtained 0·13618 as the specific heat of zinc chloride. He however made only one determination, and used turpentine.

These facts prove, therefore, that turpentine is unsuitable for calorimetical experiments, giving results which are too high. This conclusion was further confirmed by a determination of the specific heat of zinc chloride (m. p. 265°), by means of the turpentine and petroleum calorimeters respectively; the results obtained being as follows:—

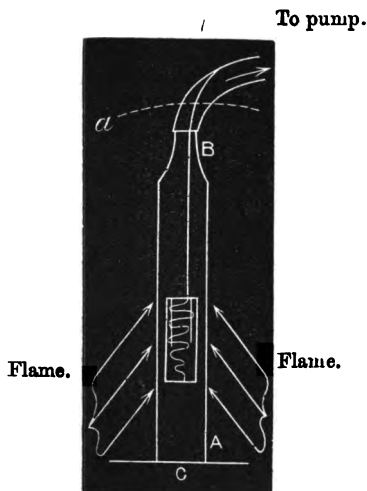
In petroleum.	In turpentine.
0.14286 at 150°	0.15005 at 151°
0.14301 at 157	0.14707 at 159
0.14327 at 240	0.14150 at 159
0.14289 at 258	0.14885 at 165
	0.14567 at 251
	0.14170 at 252
	0.14630 at 257
	0.14665 at 257

Mean .. 0.14301

Mean .. 0.14597

For the *determination of the temperature of the mercuric chloride when heated strongly under diminished pressure*, the following method was adopted:—The salt was fused on to a platinum spiral, so as to form a solid cylinder $\frac{5}{8}$ -inch diam. and 2 to 4 inches long; this was suspended freely in a vertical tube of hard glass ($\frac{3}{8}$ -inch diam.), open at one end A, and drawn out at the other B as shown in Fig. 2. The end of the tube A was ground, and could be closed with a polished plate of brass and beeswax. The end B was connected with the Sprengel pump, and the tube so arranged that the cylinder of mercuric chloride hung freely without touching the sides of the tube. The pressure was then reduced to the requisite point, and the sides of the

FIG. 2.



tube strongly heated with the flame of a Bunsen lamp. When it was thought that the salt had attained a temperature above that of its natural melting point, the lamp was extinguished, the plate C quickly removed, and the calorimeter instantly brought under the mouth of the tube, whilst an assistant cut the suspending wire at *a*. The mercuric chloride then dropped into the calorimeter, which was at once removed, and the temperature was registered in the ordinary way.

The calorimetrical temperatures attained by the mercuric chloride, when heated to a known temperature (as indicated by a thermometer) under ordinary pressure, or when heated as strongly as possible under diminished pressure, were as follows, using in all cases the value 0.064 as the specific heat of mercuric chloride.

Under Ordinary Pressure.

In petroleum.		In turpentine.			
Temperature as indicated by		Series (1).		Series (2).	
		Temperature as indicated by		Temperature as indicated by	
Thermometer.	Calorimeter.	Thermometer.	Calorimeter.	Thermometer.	Calorimeter.
240	240	230	251	152	158
244	244	240	251	168	175
247	247	250	268	191	198
248	248	266	280	209	218
253	249			241	258
				253	262

Under Diminished Pressure.

In petroleum.		In benzene.		In turpentine.		
Temperature by cal.	Pressure.	Temperature by cal.	Pressure.	Temperature by cal.	Pressure.	
278	300	268	270	308	318	M.p. of HgCl_2 . = 269 uncorr. = 277 corr.
274	310			338	328	
				359	?	
				374	340	
				389	312	
				401	318	
				408	340	

These figures show that when the temperature of the mercuric chloride is indicated by dropping into a benzene or petroleum calorimeter, normal results are obtained which are either identical with the temperatures indicated by a thermometer or are not above 277° , the natural melting point of mercuric chloride, whilst when the temperature is indicated by dropping into a turpentine calorimeter, abnormally high results are obtained, which are always above those indicated by a thermometer, or above the ordinary melting point of mercuric chloride.

GENERAL RESULTS.

(M. p. of mercuric chloride used in the experiments = 277° corr.).

(1.) When mercuric chloride is strongly heated under pressures less than the critical pressure, then the temperatures attained by the salt as indicated (a) by a thermometer, (b) by a turpentine calorimeter, (c) by a petroleum or benzene calorimeter, are as follows:—

- a. *By Thermometer.*—When the salt is in the form of a compact powder, the temperature rises 21° , and sometimes as much as 50° and more above the melting point of the mercuric chloride. When the salt is in the form of a resolidified cylinder, the temperature rises to 15° above the melting point, the bulb and lower portions of the stem being in all cases completely covered by the salt.
- b. *By Turpentine Calorimeter.*—The temperature rises to as much as 100° above the ordinary melting point.
- c. *By Petroleum or Benzene Calorimeter.*—The temperature cannot be obtained above the ordinary melting point, but is generally a few degrees less.

The high temperatures registered by the turpentine calorimeter are fallacious, because the hot mercuric chloride on coming in contact with the turpentine probably produces more chemical change in the latter. The high temperatures indicated by the thermometer are possibly due to the diffusion of the superheated vapours of the mercuric chloride through the pores of the solid salt. The fact that higher results are obtained with the compressed powder than with the resolidified massive compound, is probably owing to the former being more porous than the latter.

The general conclusion then is, that though mercuric chloride does not fuse when heated under pressures less than the critical pressure, yet it cannot be obtained in the solid state at temperatures appreciably above its ordinary melting point, the whole of the heat applied being absorbed as latent heat in the conversion of the solid directly into the gaseous state.

(2.) Turpentine cannot safely be used in a calorimeter for the determination of the specific heats of bodies soluble in water, since some substances, such as the chlorides of zinc and mercury, cause an evolution of heat in the calorimeter, due probably to some chemical action on the turpentine. Hence many of Regnault's specific heat determinations of bodies soluble in water, and for which he used turpentine, are probably a little too high, being in almost all cases higher than the corresponding numbers obtained by Kopp, who used coal-tar naphtha.

A comparison of Regnault's and Kopp's results shows, in fact, that in 12 out of 16 cases in which the former used turpentine, higher results were obtained than those of the latter, who employed coal-tar naphtha, whilst in one case they are identical.

Regnault's results, on the average, are nearly 3 per cent. higher than Kopp's. In my own experiments turpentine gives results rather over 2 per cent. higher than petroleum in the case of zinc chloride, and rather less than 8 per cent. higher in that of mercuric chloride.

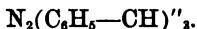
(3.) The specific heat of mercuric chloride is 0.06425, and that of zinc chloride 0.14301, as found in a petroleum calorimeter. The specific heat of neither salt alters with rise of temperature, at any rate between 0—150° and 0—250°.

L.—On the Constitution of Amarine and Lophine.

By FRANCIS R. JAPP, M.A., Ph.D., Assistant Professor of Chemistry in the Normal School of Science, South Kensington, and H. H. ROBINSON.

THE compounds amarine and lophine were discovered independently by Laurent and by Fownes between the years 1841 and 1847. Laurent obtained amarine, which has the formula $C_{21}H_{18}N_2$, by saturating an alcoholic solution of benzaldehyde with ammonia. Fownes prepared it by boiling the isomeric hydrobenzamide with caustic potash. Lophine, which has the formula $C_{21}H_{16}N_2$, and is therefore distinguished from amarine by containing in its molecule two atoms fewer of hydrogen, was obtained by Fownes in the destructive distillation of amarine, and by Laurent in the destructive distillation of hydrobenzamide. This latter compound had been discovered in 1836 by Laurent, who obtained it by the action of aqueous ammonia upon benzaldehyde. Owing to the readiness with which it is decomposed by acids into

its generating substances, benzaldehyde and ammonia, most chemists have agreed to regard it as possessing the constitution



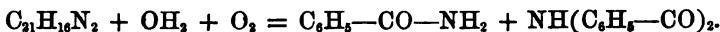
In spite of the labours of numerous investigators, nothing definite was for a long time known concerning the constitution of amarine and lophine. Quite recently, however, the problem has been attacked with greater success by Emil Fischer and H. Troschke (*Ber.*, 13, 706), though these authors are unable to give more than partially developed constitutional formulæ for lophine and amarine. As the constitutional formula for lophine suggested the work described in the present paper, we will give the reasoning of Fischer and Troschke in detail.

The new experimental facts upon which these authors sought to base a constitutional formula for lophine were the following:—

1. Lophine may be obtained from amarine by the removal of two atoms of hydrogen by oxidation:—



2. By careful oxidation lophine is converted into a mixture of benzamide and dibenzamide according to the equation:—

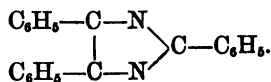


3. Lophine yields a bromine addition-compound (formula uncertain).

4. Lophine possesses a vapour-density corresponding with the molecular formula $\text{C}_{21}\text{H}_{16}\text{N}_2$.

We will give a translation of the authors' discussion of these results:—

"From the foregoing experiments we may conclude with certainty that lophine is not a compound of the diphenyl type, but contains three intact phenyl-groups. There therefore remains a lateral group consisting of three atoms of carbon, two of nitrogen, and one of hydrogen. In this group the three carbon-atoms are attached to nitrogen, as is proved by the simultaneous formation of dibenzamide and benzamide by oxidation. A little reflection further shows that two of the carbon-atoms must be directly united to each other, as in dibenzyl or stilbene. Finally, the remarkable stability of the whole group renders it probable that we have here a closed ring consisting of three atoms of carbon and two of nitrogen, as represented by the formula—

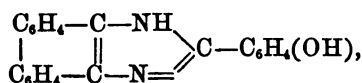


"As regards the position of the last hydrogen-atom and the arrangement of the remaining bonds in the ring, the existing ex-

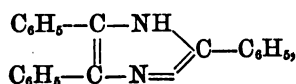
perimental material affords no safe criterion. At all events the ring must contain either four free affinities or two cases of double bonds, in order to account for the ready addition of bromine.

"Amarine appears to contain a similar nucleus, to which two additional atoms of hydrogen are attached."

Between the above partially developed formula for lophine and the formulæ of the compounds recently obtained by one of us in conjunction with Mr. Streatfeild (this Journal, *Trans.*, 1882, 149), by the action of hydroxyaldehydes and ammonia upon phenanthraquinone, there is an unmistakable resemblance. Thus with salicylaldehyde and parahydroxybenzaldehyde, two compounds were obtained of the formula—



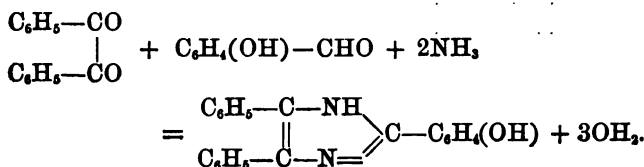
ortho and para respectively. Now, if we complete in the same sense Fischer and Troschke's partial formula for lophine, by introducing at corresponding points of the C and N ring the missing hydrogen-atom and the two cases of double bonds, thus:—



we arrive at the formula of a compound from which the preceding differs only in being a phenanthrene-derivative instead of a stilbene-derivative, and in containing a hydroxylated instead of a non-hydroxylated phenyl-group.

It appeared to us that the validity of these conclusions would be established could we succeed in synthesising lophine by a reaction similar to the above, substituting benzil for phenanthraquinone.

We hoped, therefore, by the action of a hydroxybenzaldehyde on benzil in presence of ammonia, to obtain hydroxylophine according to the equation—



(Cf. this Journal, 1882, 155.) From this hydroxylophine ordinary lophine might be obtained by replacing the hydroxyl-group by hydrogen.

(With the non-hydroxylated aldehydes, it will be remembered, compounds were obtained in the phenanthraquinone reaction containing only one nitrogen-atom in the molecule, and belonging to a different class from the above (*ibid.*).

Action of Parahydroxybenzaldehyde upon Benzil in Presence of Ammonia.

Parahydroxybenzaldehyde was selected for this reaction in preference to salicylic aldehyde, for the reason that in the phenanthrene series the para-compound is more readily purified by means of its solubility in caustic alkalis, and, what is more important, is more easily reduced by zinc-dust than the corresponding ortho-compound.

34 grams of benzil and a little more than the molecular proportion (somewhat over 20 grams) of parahydroxybenzaldehyde were introduced into a soda-water bottle and heated under pressure with a large excess of concentrated aqueous ammonia at 100° for one hour. At the end of that time the solid substance had fused together to a white mass, in which no trace of the yellow colour of the benzil was visible. That no benzil had remained unaltered was evident from the fact that the product was soluble without residue in dilute caustic alkalis.

The product was now powdered and boiled with water, which removed a small quantity of colouring matter. It was then dissolved in alcohol, with which it yielded a faintly yellow-coloured solution. To the boiling alcoholic solution water was added, but not in quantity sufficient to produce a permanent turbidity. On cooling, the new compound was deposited from the dilute alcoholic solution in tufts of colourless needles. By repeated crystallisation from alcohol (in subsequent crystallisations without dilution) it was obtained perfectly pure. The fusing point exhibited an anomaly: the pure substance fused at 254—255°, but, after allowing it to solidify in the capillary tube, it was found to fuse the second time at 258—259°. Analysis yielded results agreeing with the expected formula $C_{21}H_{18}N_2O$:—

	Substance.	CO ₂ .	OH ₂ .
I	0.1562	0.4616	0.0720
II	0.1974	0.5846	0.0910

III. 0.1001 gram burnt with copper oxide in a vacuum gave 8.02 c.c. moist nitrogen at 20.7° and under 767.2 mm. pressure, corresponding to 0.0092 gram nitrogen.

	Calculated for $C_{21}H_{16}N_2O$.		Found.			Mean.
	I.	II.	I.	II.	III.	
C_{21}	252	80.77	80.59	80.77	—	80.68
H_{16}	16	5.13	5.12	5.12	—	5.12
N_2	28	8.97	—	—	9.22	9.22
O	16	5.13	—	—	—	(4.98)
	312	100.00				100.00

The substance employed in analysis was dried at 140° . At 80° it obstinately retains alcohol.

The substance is almost insoluble in benzene, ether, and chloroform, very soluble in acetone. Hot dilute caustic soda dissolves it readily, and from the solution the sodium salt crystallises on cooling in fine flexible needles. Carbonic anhydride precipitates the substance from the alkaline solution. It is insoluble in hydrochloric acid.

Acetyl-derivative.—A portion of the above compound was heated with an excess of acetic anhydride at 150° for five hours. On cooling, the tube was filled with tufts of needles closely resembling in appearance the original compound. After washing with alcohol and drying, they possessed a faint satiny lustre. They were recrystallised from boiling alcohol, in which they are much less soluble than the original compound, and were thus obtained with the fusing point 229° , which did not alter on further recrystallisation. Analysis gave figures corresponding to the formula of a monacetyl-derivative,



	Substance.	CO_2 .	OH_2 .
I	0.1803	0.5148	0.0840

II. 0.0936 gram burnt with copper oxide in a vacuum gave 6.68 c.c. moist nitrogen at 21° and under 770.7 mm. pressure, corresponding to 0.0077 gram nitrogen.

	Calculated for $C_{23}H_{18}N_2O_2$.		Found.	
	I.	II.	I.	II.
C_{23}	276	77.97	77.87	—
H_{18}	18	5.08	5.18	—
N_2	28	7.91	—	8.24
O_2	32	9.04	—	—
	354	100.00		

Reduction of the Compound, $C_{21}H_{16}N_2O$.

A quantity of the compound was mixed with 30 times its weight of zinc-dust and distilled from combustion tubing. The temperature was

kept below redness and the distillation was conducted in a current of hydrogen. The distillate solidified in needles, to which a small quantity of greenish oily matter adhered. The latter was removed by washing with ether, the solid portion was dissolved in boiling alcohol, and the solution decolorised with animal charcoal. On cooling, tufts of long needles were deposited. These, after two or three crystallisations, fused at $267-270^{\circ}$, the fusing point of lophine, and, like lophine, possessed a lustre resembling that of caffeine. Analysis gave figures agreeing with those required by lophine:—

	Substance.	CO ₂ .	OH ₂ .
I	0.0973	0.3041	0.0478

II. 0.0954 gram burnt with copper oxide in a vacuum gave 7.78 c.c. moist nitrogen at 19.7° and under 774 mm. pressure, corresponding to 0.0091 gram nitrogen.

	Calculated for C ₂₁ H ₁₆ N ₂ .		Found.	
			I.	II.
C ₂₁	252	85.13	85.23	—
H ₁₆	16	5.41	5.46	—
N ₂	28	9.46	—	9.51
	296	100.00		

The lophine thus obtained could not in any way be distinguished from that prepared by the distillation of hydrobenzamide. The compound C₂₁H₁₆N₂O is therefore *parahydroxylophine*.

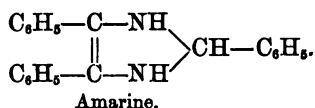
If, therefore, the mechanism of the reactions with aldehydes in presence of ammonia is to be regarded as the same in the case of benzil and in the case of phenanthraquinone—and everything appears to point to such an identity—the above synthesis leads to the adoption for lophine of the constitutional formula given at the beginning of this paper. Lophine would thus belong to the class of Hübner's anhydro-bases. It would be, to employ Hübner's nomenclature, *anhydrobenzoyldiamidostilbene*. It would resemble Hübner's compounds, inasmuch as the two amido-groups with which the condensation occurs are attached to two adjacent carbon-atoms, but would differ from them, inasmuch as these carbon-atoms do not form part of a benzene nucleus.

Both lophine and the anhydro-bases are monacid bases. Lophine also resembles the anhydro-bases in its behaviour with the iodides of the radicles of the methyl series: thus, by the action of ethyl iodide, Kühn (*Annalen*, 122, 327) has prepared *diethyllophinium iodide*, C₂₁H₁₆(C₂H₅)₂N₂I, corresponding to Hübner's *diethylanhydrobenzoyl-*

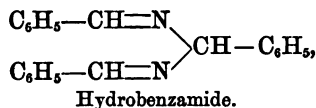
diamidobenzene iodide, $C_{13}H_9(C_2H_5)_2N_2I$,* both lophine and anhydrobenzoyldiamidobenzene displaying the entire behaviour of secondary amines.

As regards the construction of a constitutional formula for amarine, we have three facts to guide us: (1) the formation of lophine from amarine by the removal of two atoms of hydrogen during oxidation; (2) the existence of a diethylamarine, obtained by the action of ethyl iodide upon amarine (Borodin, *Annalen*, 90, 78), and (3) the formation of a nitrosamine when amarine is treated with nitrous acid (Borodin, *Ber.*, 8, 933).

Starting, therefore, from a lophine of the formula given in this paper, the above facts would be most simply accounted for by ascribing to amarine the formula



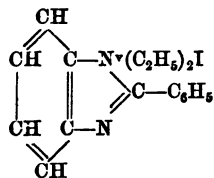
This formula further expresses in a simple manner the intramolecular re-arrangement which occurs when the neutral substance hydrobenzamide—



is converted by heating to 120—130°, or by boiling with caustic alkalis, into the isomeric basic compound amarine.

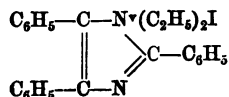
We intend to study the action of other aldehydes upon benzil in presence of ammonia, and in this way to prepare if possible fresh analogues of lophine. The reaction would probably also occur with other compounds of the benzil type, such as cuminil.

* Supposing lophine to possess the constitution here attributed to it, the constitutional formulæ of these two compounds would be—



Anhydrobenzoyl-
diamidobenzene
iodide.

and



Diethyllophinium
iodide.

LI.—*On Rotary Polarisation by Chemical Substances under Magnetic Influence.*

By W. H. PERKIN, F.R.S.

A SHORT time since, whilst working with the isomeric methylcoumaric acids, I was induced to examine some of the physical properties of a few of their derivatives side by side, and amongst others the power possessed by their ethers of rotating the plane of polarisation when under magnetic influence. Still later I made similar experiments with the methylic and ethylic ethers of citraconic and mesaconic acids. The results of these observations showed that the corresponding ethers of these substances, although of the same composition and apparently the same chemical constitution, gave somewhat different measurements, the more stable bodies giving the higher numbers.

Since Faraday's discovery of magnetic rotary polarisation in 1845 numerous experimenters have worked in this direction, but it will not be necessary for me to enter into the history of the subject, as it has already been so ably given by De la Rive (*Ann. Chim. Phys.*, 1868, 15, 57) and Becquerel (*Ann. Chim. Phys.*, 1877, 12, 1), in their important memoirs.

So far as the subject has been studied by previous workers no definite relationship between the chemical composition of substances and their power of rotating the plane of polarisation when under the influence of magnetism has been observed. Having already worked a little on this subject, I was induced to extend my experiments, and try to discover if possible whether any relationship of this kind existed.

The apparatus I employed was similar to that used by Becquerel (*Ann. Chim. Phys.*, 1877, 12, 12), except that the magnet at my disposal was not nearly so powerful. I generally used tubes about 10 cm. in length, closed at the ends with glass plates, to hold the substances under examination, the ends of the tubes being inserted a short distance into the perforations in the armature, as proposed by De la Rive. Water and carbon disulphide were used as standards, observations being usually made with one of these before and after the examination of any substance, so as to correct for any alteration in the power of the magnet during the experiment.

In calculating his results De la Rive took the relationship which he found to exist between the magnetic rotary power of a body and that of distilled water, which served as unity, and called the numbers thus obtained, the specific rotary power. Becquerel, on the other hand,

took carbon disulphide as unity, and then further calculated out the result in connection with the index of refraction of the body.

The results I have obtained agree pretty closely in most cases with those of De la Rive and Becquerel, but seem to bear little or no relationship to the chemical composition of the substances examined. It was, however, soon seen that by calculating the differences between the magnetic rotary effect of unit-lengths of fluid bodies no useful result could be expected. Take for example the examination of bodies belonging to the homologous series: it is evident that as one ascends in the series the effect on a unit-length for the addition of CH_2 in the molecular composition would become smaller and smaller, and consequently the difference in the measurement, if differing regularly with the composition, would decrease in the same way, and this is seen to be the case: thus in the measurement of the iodides of the alcohol radicals (compared with water as unity) the difference between methyl and ethyl iodide is about 0.334, whilst that of ethyl and propyl iodide is about one-third lower, viz., 0.227.

From a chemical point of view it is therefore evident that a comparison of unit lengths of fluid bodies cannot show any clear relationship to their chemical composition. This, however, would not be the case if unit-lengths of vapours were examined, because they would be occupied by equal numbers of molecules.

Becquerel has devised a beautiful and elaborate apparatus for the examination of the rotary magnetic power of gases (*Ann. Chim. Phys.*, 1880, 21, 289), which will give an idea of what would be required for the examination of substances in the state of vapour. It will be seen that, from its dimensions and the difficulties there would be of keeping up uniform temperatures, &c., in such an apparatus, it would be almost impossible to examine the greater number of bodies in the state of vapour. It is possible, however, to refer the results of the observations obtained by the examination of unit-lengths of fluids to the lengths of columns of liquids, which would be formed by the condensation of unit-columns of their vapours, in other words to lengths related to each other in proportion to their molecular weights, making the necessary correction for difference of densities. This may be found by the simple formula—

$$\frac{r \times M_w}{d},$$

r being the rotation observed, M_w the molecular weight, and d the density. This calculation having been made both for the substance under examination, and also for the standard with which it is to be compared, it is only necessary to divide the result obtained from the former by that of the latter, and the result will be the "molecular

coefficient of magnetic rotation," or more briefly the "molecular rotary power."

On calculating out the results of experiment in this way, taking water as unity, the numbers obtained clearly indicate that the molecular magnetic rotary power of bodies follows with the chemical composition in a regular, or comparatively regular, manner. This will be seen from the results I obtained on the examination of the iodides of the alcohol radicals.

Substance.	Molecular rotatory power.	Diff. for CH ₂ .
Water.....	1.00	
Methyl iodide	9.07	} = 1.12.
Ethyl " 	10.19	
Propyl " 	11.39	} = 1.20.
Amyl " 	13.4	
		} = 2.00 = 1.0 × 2.

The molecular rotary power of ethylic iodide calculated from the average of two of De la Rive's measurements, is 10.1 (*Ann. Chim. Phys.*, 1871, 22, 12 and 18).

From this table it will be seen that for every addition of CH₂ there is a variation of from 1.0 to 1.2.

Fortunately Becquerel has examined a corresponding series of alcohols (methylic excepted) to the above (*Ann. Chim. Phys.*, 1877, 12, 37). De la Rive has examined ethylic and amylic alcohols. I have also examined methyl and ethyl alcohols. The molecular rotatory power of these bodies, calculated from these various results, are as follows, water being taken as unity.

	Becquerel.	De la Rive.	Perkin.	Average.	Diff. for CH ₂ .
Methyl alcohol. . . .	—	—	1.62	1.62	} = 1.06.
Ethyl " 	*2.64	2.78	2.63	2.68	
Propyl " 	3.74	—	—	3.74	} = 1.14.
Butyl " 	4.88	—	—	4.88	
Amyl " 	6.06	5.95	—	6.00	} = 1.12.

In this series we therefore find that the difference for CH₂ is practically the same as for the iodides, and even within smaller limits.

Some time since a specimen of amylene was examined in reference to its magnetic rotary power. This substance is of interest in connection with the above results, because C₅H₁₀ represents CH₂ × 5. The molecular rotatory power calculated from the numbers obtained is 5.87. This it will be observed is only a little in excess of the value of five times CH₂, which, taking an average of the above numbers, would be 5.5.

* In Becquerel's paper there is evidently a misprint, ethyl alcohol being called methyl alcohol.

Some slight differences besides experimental errors most probably exist in the numbers given in the foregoing series, arising from the fact that all the bodies examined are not primary ones. The iodide of amyl used, for example, was the iso-compound, and it is most probable also that the butyl and amyl alcohols examined by Becquerel were likewise the iso-compounds.

De la Rive first showed that isomeric and metameric bodies gave somewhat different rotation when under magnetic influence. In his paper already referred to he gives the results he obtained on examining amyl alcohol (iso?) and Würtz's amylene hydrate, and he found the latter to give a slightly lower number than the former. The molecular rotary powers calculated from his numbers are as follows:—

Amyl alcohol.....	5.95
Amylene hydrate	5.81
	<hr/>
	0.14 diff.

Judging from this example the results given in this paper are not very seriously affected by some of the bodies belonging to isomeric series.

I have noticed the effect of isomerism on magnetic rotation by examining the chlorides of ethylene and ethylidene, the latter giving the lower number. This part of the subject is of considerable interest, and will require careful study. As mentioned in the commencement of this paper, the so-called physical isomerides differ slightly in their magnetic rotary power.

With reference to the aromatic series of bodies, little as yet has been done, the only measurements of definite bodies which have been published are those of benzene, toluene, and xylene, by Becquerel. I have also examined these and other hydrocarbons, but I do not now propose to discuss this subject, as I feel the facts at present known are too few to generalise from. The study of the aromatic series, however, promises to be of considerable interest. So far as experiments have been made, considerable differences appear to exist between ortho-, meta-, and para-compounds, and until this part of the subject has been investigated very little can be done in other directions, such as the replacement of hydrogen by alcohol radicals, &c.

I have lately obtained a more powerful electromagnet, and propose continuing my experiments in the different directions indicated in this paper, as it appears that results are likely to be obtained which will be found of practical value to chemists.

LII.—*A Spectroscopic Study of Chlorophyll.*

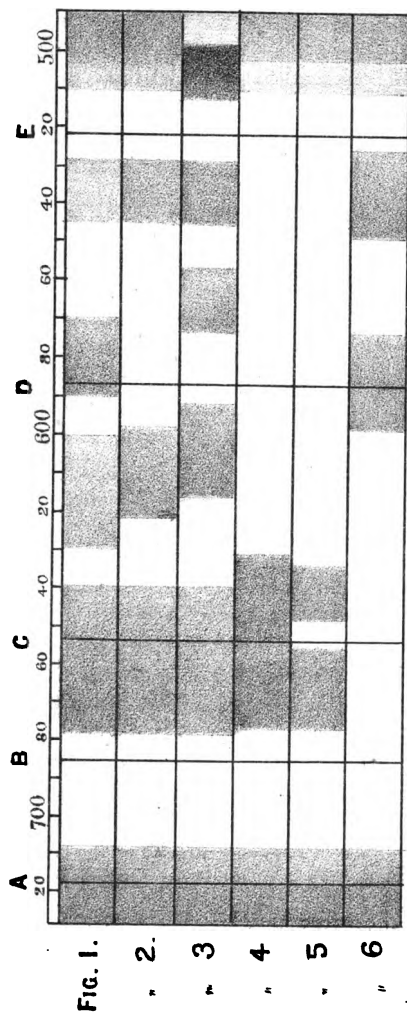
By W. J. RUSSELL, Ph.D., F.R.S., and W. LAPRAIK, F.C.S.

THE study of chlorophyll has great fascination ; it also has its difficulties. We did not propose adding to the many elaborate attempts to isolate and purify this body ; but the beauty and definite character of the spectrum which it gives induced us to try whether some insight into its character and constitution could not be obtained from the study of the spectroscopic changes which it can be made to undergo ; and as one of us has already shown that in the case of the cobalt salts, the spectroscope enables us to follow many chemical changes, we thought that it might be possible to interpret the spectroscopic changes of chlorophyll, and so gain some knowledge of the properties and nature of this body.

The extraction of the green colouring matter from leaves was effected in most cases by breaking up the leaves in a mortar with a mixture of two parts of alcohol and one of ether. The colour of the liquid thus obtained is of a dark green, varying in shade according to the nature of the leaves used, and the solution always has the well-known red fluorescence. This liquid, when examined spectroscopically, gives what is known as the chlorophyll spectrum. According to Krauss, it consists of seven bands ; the three at the most refrangible end of the spectrum are difficult, as Krauss says, to observe, and with our source of light, a gas-flame, we could see in an ordinary chlorophyll solution little or nothing of them ; but under special circumstances, which will be described further on, the least refrangible of the three becomes very visible. We have confined our observations principally to the four least refrangible bands. Other solvents, such as chloroform, disulphide of carbon, benzene, &c., were used occasionally ; they give a similar spectrum, but in most cases they do not dissolve the colouring matter so readily as alcohol and ether do. The ethereal solution appears always to give a clearer and more brilliant spectrum than the alcoholic solution. Fig. 1 shows the spectrum of the solution obtained as above described from the majority of the leaves we have examined.

Among common outdoor plants, the vine and the Virginian creeper may be cited as apparent exceptions, giving a different spectrum. (Fig. 2.) The second band in this case has moved towards the more refrangible end of the spectrum, the band from 589 to 573 has disappeared, and now there is a very marked band from 545 to 532. The cause of this change in the spectrum we shall explain further on.

Fig. 1 then, as far as it goes, represents the spectrum given by the



alcohol and ether extract of most leaves. It is important at once to give a definite meaning to the term chlorophyll, and we would therefore state that we mean by it the body or bodies capable of giving this particular spectrum, and of course we found our conclusions on the assumption that a particular absorption-spectrum is a complete identification of a substance.

As is well known, the exact position of these bands alters with the solvent used; in all cases, when no mention is made to the contrary, a mixture of alcohol and ether is the solvent we have used. Apparently the statement that the higher the specific gravity of the solvent, the nearer are the bands to the red end of the spectrum, is not in all cases true, for we find that the chlorophyll bands are nearer to the red in carbon disulphide than in chloroform. All our observations have been made with a Dasaga's spectroscope having a single heavy glass prism, and the position of the bands is given in millionths of a meter, reduced from the observations by graphical interpolation. Captain Abney has also been kind enough to take photographs of the different spectra, and these agree with our eye observations. They also prove that there are no bands in the ultra-red.

The first point we would note with regard to chlorophyll is that, as far as our experiments go—and we have now tried a large number of different leaves—although there are apparent exceptions, this particular substance we call chlorophyll exists in all green leaves.

If thinner and thinner strata, or more and more dilute solutions of the same thickness be examined, the fainter bands are seen gradually to fade out, and what is of importance, the dominant band, the last to disappear, thins out to a band from 670 to 660.

Passing over a large number of experiments on other points, we shall limit our present communication as far as possible to an account of the action of acids and alkalis on this so-called chlorophyll.

It is a body exceedingly sensitive to the action of acids. If for instance a mere trace of hydrochloric acid gas be introduced into the air of a test-tube containing a chlorophyll solution, on shaking the tube, the 628 band will be found to have moved slightly towards the blue, and the next band to have become fainter. This action of the acid, specially with regard to the 628 band, is very remarkable; the addition of acid gradually causes this band to move bodily towards the blue, till it reaches 611—589. So constant and complete is this action, that the position of the band is an indication up to a certain amount of the quantity of acid present. On adding a little more hydrochloric acid gas to the air of the test-tube, and again shaking, this second band will be found to have moved from 615 to 596, the 589—573 band will have disappeared, and the other band at 545—532 will remain unmoved, but will have become much darker. On still further increasing the

amount of acid, the second band comes to 611—589, and now a new band appears from 573—558, and the band at 545—532 has also again increased in intensity. Further, the blue end of the spectrum has considerably opened. This spectrum, Fig. 3, is permanent, for on adding more acid, even a large amount of liquid acid, no further alteration takes place. The action of hydrochloric acid on chlorophyll appears then to be very definite, and is well shown by the two drawings, Figs. 2 and 3, which represent two well-marked stages; in the first the movement of the 628 band and the disappearance of the 589 band, the other two bands remaining unaltered in position; in the second (Fig. 3) the 628 band has moved to its furthest extent, and a new band has appeared at 573—558, the most and least refrangible of the four bands remaining still unaltered in position.

We have described in detail these spectra, for they have great interest and importance, owing to the fact that these changes do not arise from the formation of any chlorine-compound, but are produced by the action of the hydrochloric acid simply as an acid. Substitute any strong acid, sulphuric, nitric, &c., for the hydrochloric acid, and exactly the same changes will occur: Use a weak acid, an organic acid, such as tartaric, citric, oxalic, &c., and the action does not go beyond the first stage (Fig. 2). Carbonic acid is without action on the chlorophyll.

There is also another way in which the same changes may be brought about without the presence of acid, namely, by the application of heat. If, for instance, the solution of chlorophyll be evaporated to dryness on a water-bath at a temperature of 80° or above, then on redissolution it will be found to have changed and to give no longer the original but the second spectrum. Let the evaporation take place at ordinary temperatures in a current of air, or under the air-pump, then, on at once redissolving the residue, no change will have occurred; if, however, after the evaporation, the dry mass be kept for a short time, it will change even at ordinary temperatures. Further, if the alcoholic solution be diluted with water and then boiled, the body giving spectrum No. 2 is formed; and the addition of certain salts, such as mercuric chloride, ferric chloride, &c., causes a similar change. Alum precipitates the colouring matter, and if the precipitate be collected, washed, and dried at ordinary temperatures, and again dissolved, it will give the second spectrum. On the other hand, basic acetate of lead precipitates the chlorophyll unchanged.

Acids, heat, metallic solutions, all act on the chlorophyll, and all give rise to an identical spectrum, and therefore we conclude to the same body. Further, it is of interest to note the identity of these processes with those used to coagulate albumin, and consequently the probability that the change in both cases is of a similar character.

Since these changes are produced by processes and reagents which differ so materially, we are bound to conclude that the change is a molecular, not a chemical one. In these cases the least refrangible band does not alter, for if the solution be diluted, it always thins down to a band from 670 to 660; the other three bands, on the contrary, all change, the 628—607 moving towards the blue, the 589—573 band disappearing, and the 544—531 band becoming very much darker. In fact, although a shadowy indication of this last band is constantly visible in the normal solution, it is often so small in amount that it should be regarded rather as an accidental impurity than as a necessary part of the normal spectrum. Again, the essential and characteristic distinction between the two spectra, Figs. 2 and 3, is the presence in the latter of the band at 573—558. This band, as far as we know, is produced solely by the presence of a strong acid in considerable excess, and all specimens of chlorophyll, either normal or not, yield it on the addition of hydrochloric, nitric, or sulphuric acid.

There is obviously a considerable resemblance between these three spectra, but at present, notwithstanding the beautiful work of Abney and Festing, we can hardly deduce from these indications alone the nature and relationship between these bodies; but from the processes used for obtaining them, there can, we think, be little or no doubt that they are simply molecular modifications of the original chlorophyll, and we propose at present to designate them as α - and β -chlorophyll.

With regard to the different purifying processes that have been used for obtaining chlorophyll from leaves, &c., in some cases the normal chlorophyll has been extracted; in others, the leaves have first been dried at steam-heat, or the alcoholic solution has been boiled, and it is the α -chlorophyll that has been obtained. We have tried several of these processes, and efficacious as they undoubtedly are in removing many, if not all, of the numerous bodies existing in more or less intimate connection with the chlorophyll, still they appear to produce really no change in the spectrum. With regard to general absorption, no doubt they do produce marked effects, specially at the blue end of the spectrum; this is well seen in the methods of purification recommended by Conrad. He obtained, as he believed, a separation of chlorophyll into a green and a yellow body by means of benzene. Observation shows, however, that the band-giving body, the chlorophyll, remains quite unchanged by the benzene, but that certain bodies which absorb in the blue are insoluble in this menstruum: hence the change in colour.

Hydrochloric acid has apparently considerable power of destroying certain of these blue-absorbing bodies, for on adding this acid to an ordinary chlorophyll solution, blue rays come through, where before

the addition it was quite dark. This fact has also this application: by means of it chlorophyll can be obtained more free from blue-absorbing matter than in any other way we are acquainted with. If to an alcoholic chlorophyll solution dilute hydrochloric acid be added, a precipitate is obtained, and if this be washed, dried, and dissolved in ether or in a mixture of alcohol and ether, it gives a solution which shows, not only the bands of the α -modification, but also a band at the blue end of the spectrum, which was before alluded to, quite dark and distinct from 513 to 499. In all probability this band is present in other cases, but is masked by general absorption.

The action of alkalis on chlorophyll is quite as marked and as characteristic as the action of acids. On adding either an alcoholic or an aqueous solution of potash or soda to a chlorophyll solution, two effects are produced: one is the fading out of all except the least refrangible, the dominant band, and the other is the spread of this band towards the blue, extending from 674 to 628. The action of alkali does not, however, stop here, for if a considerable excess be present, another and an exceedingly interesting change sets in, the dominant band now from 674 to 628 dividing into two distinct bands,* one from 674 to 660, and the other from 646 to 632; then if sufficient alkali be present, the 674 to 628 band gradually becomes fainter and fainter, and ultimately the one from 674 to 628 alone remains. The same changes can be brought about with the α - and β -chlorophyll, but with far more difficulty. To change these varieties the potash or soda must be stronger and the contact longer. With ammonia we believe we have broken this band up, but in almost all cases ammonia is without action on these modified chlorophylls, and it is quite clear that, as regards the action of alkalis, the α - and β -chlorophylls are far more stable than normal chlorophyll. There are other and more convenient methods for preparing this one-banded modification of chlorophyll. One is to evaporate an alcoholic solution of chlorophyll to dryness over a water-bath; then treat the residue with water, which washes out a soluble yellow substance, varying very much in amount with different samples of chlorophyll; and then evaporate the residue several times to dryness with a mixture of equal parts of ammonia and water. Another method is to act on the chlorophyll with a solution of copper sulphate; the precipitate formed is washed with water until all the copper is removed, then dried, and dissolved in alcohol and ether. It gives a spectrum identical with that obtained by the ammonia process, and like it the band is capable of being split up into two bands. In the filtrate from the above precipitate there is always much chlorophyll remaining, but this, curiously enough, has also been modified, and

* Chautard as long ago as 1836 mentions this; he naturally concludes that it is the original dominant band split up (*Compt. rend.*, 76, 570).

now gives only the one-band spectrum. When we first obtained this one-banded substance, the position of this band appeared so nearly to correspond with that of the dominant band in a strong solution, that we were inclined to believe that we had really separated the bodies giving the more refrangible bands, from those which give the less refrangible; but evidently this is not the case; neither does it now seem at all probable that such a separation would be possible.

We have used the term one-banded modification of the chlorophyll, and are aware of the possible ambiguity, that this band can be split into two; but this change is really brought about only by the continued action of alkalis, for on simply diluting the solution down even to the vanishing point of the band, there is no indication of two bands being present.

The solution of this one-banded substance is still of a beautiful green colour, and is very remarkable for its stability: neither a trace nor an excess of acid of any kind produces any change in its spectrum, and it may even be dissolved in strong sulphuric acid and reprecipitated by water without alteration.

If the action of caustic potash or soda be pushed to an extreme, for instance if chlorophyll be heated with solid potash, then it is apparently completely decomposed, the dominant band disappearing, and two bands different in position from any of the former ones being produced; these are shown in Fig. 6.

To return now to the fact of different leaves giving different spectra; for instance, when vine-leaves are treated with alcohol and ether, the liquid gives strongly the α - not the normal spectrum. As is well known, the juices of the vine-leaf are very acid: consequently during the extraction of the colouring matter, the acid has time and opportunity for action, and hence the cause of what appears at first to be an anomaly. In the leaf itself the chlorophyll is in the normal condition, for if to the bruised leaf precipitated calcium carbonate or carbonate of soda be added, together with the alcohol and ether, the filtered liquid then gives, not the α - but the normal spectrum; and even without the addition of the calcium carbonate, on rapidly extracting the colouring-matter from the leaf and examining it immediately, the spectrum is normal. It is therefore evident that although both chlorophyll and acid are present in the leaf, they are not under such conditions that they can act on one another; but bring them into solution, and the change commences immediately.

Virginian creeper, *Bignonia*, and other leaves act exactly like the vine. The acid in the *Bignonia* can be entirely removed by water, and if the colouring matter be then extracted, it gives the normal spectrum.

The way we now generally adopt in extracting the chlorophyll

from leaves is to add with the alcohol and ether precipitated calcium carbonate; then, whether the juice of the leaf be very acid or not, is a matter of indifference. We have already stated that in all the different leaves which we have examined, the chlorophyll has been found to be in the normal condition. This applies of course only to freshly gathered leaves; the chlorophyll in gathered leaves gradually changes, and passes over the α -modification, the time required for this change varying with the leaf and with external circumstances; whether the leaf be exposed to light or kept in the dark, does not appear to affect the result. Pear leaves, after being gathered for three weeks and kept in a dry room, yielded both normal and α -chlorophyll; the change apparently had just begun. The chlorophyll in some vine leaves that had been gathered less than ten days had completely passed over to the α -modification; but similar leaves, gathered at the same time and kept in water, gave only normal chlorophyll. Remembering how easily the solid normal chlorophyll passes over to the α -modification, it is evidently not necessary to suppose that the acid in the leaf is the cause of this change.

The chlorophyll having passed over to the α -modification, remains with wonderful pertinacity in the dead leaf. Dead pear leaves which had fallen from the tree seven months ago, still gave a brilliant spectrum of α -chlorophyll, and even an alcoholic and ether extract of tobacco gives this spectrum.

The solutions of chlorophyll obtained by the direct treatment of leaves with alcohol and ether, contain a large number of substances, and the chlorophyll, as well as the other bodies, undergoes change on keeping. The length of time during which these solutions retain their green colour varies very much; expose them to light, and the rapidity of the change is enormously increased. If acid be present in the solution, the chlorophyll quickly passes over to the α -modification, and even if the extract has been made with calcium carbonate present, the same change occurs, only more slowly. These changes take place even in the dark. Besides this change of the chlorophyll, other and more complicated changes occur. Solutions from some leaves can be kept in the dark apparently without change for months, whereas others rapidly alter, and the chlorophyll disappears from them. The extract from rhubarb, for instance, very soon changes, the solution becoming of a tolerably bright red colour, and the chlorophyll bands disappearing. This red substance and the other products of decomposition from their solutions do not give visible spectra, and the same remark applies to at least the majority of the colouring matters in flowers. If these green solutions be exposed to light, they are, without exception, rapidly decomposed, and lose entirely their green colour, becoming either red, yellow, or of some intermediate shade. Brilliant

sunshine in an hour or two will completely decompose all the chlorophyll in a dark green solution, not even a vestige of the dominant band remaining. If a solution of the α -chlorophyll, dissolved in alcohol and ether, be exposed to light, it is far more difficult of decomposition, and will withstand its action for a few days. That this stability is not due to the absence of certain substances in the solution of the α -modification, is shown by dissolving some of this modified chlorophyll in a normal and readily decomposable solution, when it will be found that, although there will be a change of colour owing to the decomposition taking place in such a solution, still the green colour from the modified chlorophyll will long remain. A single drop of hydrochloric acid added to the green extract, although it at once changes the bright green to a darker and browner green, enables the solution to resist this action of light to a much greater extent than it could have done if no acid had been added.

In the one-banded modification of chlorophyll we appear to have a body on which light has no action; solutions of this body have been, for the last three months, exposed continuously to all the light and sunshine we could get, and they are unchanged in colour and constitution; another proof of the really wonderful stability of this substance. Again, as a confirmation of the properties and formation of this form of chlorophyll, a single drop of sulphate of copper added to an ordinary chlorophyll extract renders the green colour of the solution permanent.

The very striking change of tint which occurs when a strong chlorophyll solution is very considerably diluted, whereupon it changes from a dark to a light yellowish-green, forcibly suggests to us the probability that the difference in shade of old leaves as compared with young ones, is due to the same cause, namely, the greater or smaller amount of chlorophyll in a given area.

LIII.—*On the Precipitation of the Alums by Sodid Carbonate.*

By EDMUND J. MILLS, D.Sc., F.R.S., and R. L. BARR.

THE behaviour of a solution of alum towards sodic carbonate is a subject of considerable theoretical as well as technical importance, and extremely complicated in its nature. It therefore appeared to us that the following research—dealing, as it does, with a specific phase of the general investigation—might be of interest to chemists.

We have been induced to submit it at this time to the Society,

partly because it is complete in itself, and partly because circumstances do not permit of our pursuing it further.

The particular alums we employed were potassio-aluminic and potassio-chromic alum.

1. *Precipitation of Potassio-aluminic Alum.*

The alum employed in our experiments was an excellent commercial sample, containing scarcely perceptible traces of iron, and yielding very nearly the amount of alumina indicated by theory. An aqueous solution of this was prepared of such verified strength as to contain 1 per cent. by calculation of aluminic sulphate, or 0.2982 gram alumina in 100 c.c.

The solution of sodic carbonate was made from cleaned sodium, by reaction in a silver vessel with water, carbonation with excess of purified carbon dioxide, and evaporation at 100° , the residue being dissolved in such a proportion of water as to constitute a liquid of 0.93038 per cent. strength. This strength, considered with reference to that of the alum solution, is as $3\text{Na}_2\text{CO}_3 : \text{Al}_2(\text{SO}_4)_3$, in equal volumes.

A precipitation experiment was carried out as follows: The bottles containing the reagents, another holding distilled water, and a dry beaker, were placed in a trough of running water until their temperature became sensibly constant. The requisite quantity of sodic solution was then introduced, with frequent stirring, into the beaker; next, sufficient water to make up an invariable volume of 100 c.c.; and lastly and always, 100 c.c. of alum solution. The mixture was well agitated with a thermometer (whose indication was observed) and left at rest, under the same conditions, for exactly an hour. At the end of this time it was filtered as rapidly as possible with the aid of suction. The precipitate was washed, first with cold, and subsequently with hot water, until the precipitate was free from sulphate; it was then re-dissolved as chloride, and precipitated by ammonia. The results of our experiments are recorded in the following table:—

TABLE I.

Potash alum taken in c.c.	Sodic carbonate taken in c.c.	Alumina precipitated.	Temperature.
100	20	0.0074 gram.	9.8°
"	30	0.0386 "	8.8
"	40	0.0979 "	9.8
"	45	0.1331 "	9.8
"	50	0.1664 "	9.9
"	60	0.2199 "	8.8
"	65	0.2472 "	10.8
"	70	0.2679 "	10.2
"	80	0.3039 "	8.9

We noticed in the course of this work that the first filtrate became turbid on standing, where lower quantities of carbonate had been added.

2. *Precipitation of Potassio-chromic Alum.*

This alum was prepared by ourselves, and recrystallised from water below 50° C., until it furnished on analysis very nearly the theoretical quantity of chromic oxide. The standard solution of this contained 1.1518 per cent. chromic sulphate, corresponding to 0.4474 gram oxide in 100 c.c. This strength, considered with reference to that of the sodic solution, is as $\text{Cr}_2(\text{SO}_4)_3 : 3\text{Na}_2\text{CO}_3$, in equal volumes.

The experiments were carried out exactly as in the case of the preceding alum; their results are stated in Table II.

TABLE II.

Chrome alum in c.c.	Sodic carbo- nate in c.c.	Weight of chromic oxide in precipitate.	Temperature.
100	60	0.0146	7.7°
"	65	0.0491	7.9
"	70	0.0979	7.7
"	75	0.1520	8.7
"	85	0.2602	8.7
"	95	0.3328	7.9
"	100	0.3566	6.3
"	110	0.3894	5.8

The first filtrate always became slightly turbid on standing.

3. *Discussion.*

On plotting out our results, we soon found reason to believe that the precipitation of an alum by sodic carbonate—as we performed it, at least—takes place in three stages. First, a considerable addition of carbonate is necessary before any precipitation takes place at all; secondly, there is precipitation according to a continuous law, until about half the alum has been thrown down; and thirdly, the precipitation is proceeded with according to the previous law, but with altered constants.

Guldberg and Waage (*Études sur les Affinités chimiques*, 63) have given a particular relation between precipitant and precipitate, which we believe to be general, and which, with a necessary linear alteration, we have found well adapted to our numerical results.

a-Potassio-aluminic Alum.—In the stage antecedent to precipitation,

very nearly 19 c.c. are required. The first stage of precipitation is represented by the equation :

$$y = \frac{0.1491 - 0.0053250(47 - x)}{1 + 0.025380(47 - x)},$$

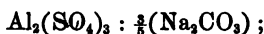
in which y is the weight of alumina precipitated, x the number of cubic centimeters of carbonate taken in any one experiment, 0.1491 represents one-half of the total alumina constantly present in the solution, and 47 is the number of cubic centimeters of carbonate required to complete the semi-precipitation.

In the second stage we have—

$$y = 0.1491 + \frac{0.1491 - 0.0045182(80 - x)}{1 - 0.0098153(80 - x)},$$

where the general symbols have the same meaning as before. The number of cubic centimeters of carbonate required for complete precipitation of all the alumina is 80.

Thus, our solution just began to yield a precipitate when the aluminic sulphate and carbonate were nearly in the ratio—



it was about half precipitated when the ratio $\text{Al}_2(\text{SO}_4)_3 : \frac{2}{3}(\text{Na}_2\text{CO}_3)$ was attained; and it was completely precipitated in the proportion $\text{Al}_2(\text{SO}_4)_3 : \frac{1}{3}(\text{Na}_2\text{CO}_3)$. This last fact is of considerable economical importance, and probably even less carbonate would have sufficed had our solutions been more concentrated.

We subjoin a numerical comparison of theory with experiment:—

TABLE III.

Carbonate in c.c.	Alumina precipitated.	Alumina precipitated, calc.
20	0.0074 gram.	0.0032 gram.
30	0.0386 „	0.0409 „
40	0.0979 „	0.0950 „
45	0.1331 „	0.1318 „
47	0.1491 „	0.1491 „
50	0.1664 „	0.1684 „
60	0.2199 „	0.2222 „
65	0.2472 „	0.2445 „
70	0.2679 „	0.2644 „
80	0.3039 „	0.2982 „

Probable error of a single comparison, 0.0025 gram.

β-Potassio-chromic Alum.—The stage antecedent to precipitation requires, in this case, no less than 59 c.c. of the sodic reagent. The

University of Michigan

subsequent stages are represented by the following equations in order:—

$$y = \frac{0.2237 - 0.0097686(81.7 - x)}{1 + 0.010083(81.7 - x)},$$

$$y = 0.2237 + \frac{0.2237 - 0.0039040(139 - x)}{1 - 0.011873(139 - x)},$$

Thus, our solution just began to yield a precipitate when the sulphate and carbonate were nearly in the ratio $\text{Cr}_2(\text{SO}_4)_3 : 2\text{Na}_2\text{CO}_3$; the stage of semi-precipitation was approximately marked by the ratio $\text{Cr}_2(\text{SO}_4)_3 : \frac{1}{2}(\text{Na}_2\text{CO}_3)$. The completion of precipitation would have required 139 c.c. carbonate. This quantity we could not hope to comprise within our conditions, though we have successfully ventured as far as 110 c.c.

TABLE IV.

Carbonate in c.c.	Chromic oxide precipitated.	Chromic oxide calculated.
60	0.0146 gram.	0.0096 gram.
65	0.0491 "	0.0519 "
70	0.0979 "	0.0979 "
75	0.1520 "	0.1483 "
85	0.2602 "	0.2596 "
95	0.3328 "	0.3325 "
100	0.3566 "	0.3568 "
110	0.3894 "	0.3922 "

Probable error of a single comparison, 0.0019 gram.

The accompanying drawing, which has been constructed from the equations, exhibits the entire course of precipitation of both oxides.

LIV.—*On the Determination of Nitric Acid as Nitric Oxide by means of its Reaction with Ferrous Salts. (Part II).*

By ROBERT WARINGTON.

THE first part of this communication having been published some time ago, a brief recapitulation of the objects and earlier stages of the investigation is probably desirable.

The method proposed by Schloesing, as specially applicable in the presence of organic matter, consists in heating the nitrate with ferrous chloride and hydrochloric acid in an atmosphere as free from oxygen

as possible, collecting the nitric oxide evolved, converting it into nitric acid by treatment with water and excess of oxygen, and estimating the nitric acid by titration with alkali of known strength. The experiments at Rothamsted have had for their object to ascertain the amount of accuracy attained by this method when applied to the determination of very small quantities of nitric acid in the presence of organic matter. In all these experiments the nitric oxide produced has been collected over mercury, and its quantity determined by gas analysis, this being, undoubtedly, the most exact method available.

In the earlier experiments (*Trans. Chem. Soc.*, 1880, 468), it was shown that some of the simpler modifications of Schloesing's process commonly employed give very low results when the amount of nitric acid present is but small, and that this error is increased by the presence of sugar. By adopting Schloesing's later improvement of conducting the reaction in a small bulb retort, through which a stream of carbonic acid could be passed, much better results were obtained. Using nitre containing 1.4 mgrm. of nitrogen, 93—94 per cent. of the nitrogen taken was obtained as nitric oxide; the presence of considerable quantities of sugar and other forms of organic matter was also now without influence. This indifference to the presence of organic matter was apparently due to the retort being heated in a chloride of calcium bath and its contents boiled to dryness in every experiment, thus ensuring a complete reaction.

The errors of deficiency still perceptible were, in all probability, due to the presence of a trace of oxygen in the retort, this oxygen being introduced in the carbonic acid gas, or in the other materials employed. The improvements to be now described consist for the most part of precautions taken to avoid as far as possible the entrance of oxygen; these improvements have been long in use in the Rothamsted Laboratory, but time has only lately been found for the execution of test experiments showing the value of the alterations made.

The apparatus now employed is quite similar to that formerly figured (*Trans.*, 1880, 477), with the only difference that the bulb retort in which the reaction takes place is now only $1\frac{1}{2}$ inch in diameter, thus more exactly resembling the form employed by Schloesing. A bulb of this size is sufficient for the analysis of soil extracts; for determinations of nitrates in vegetable extracts a larger bulb is required.

The chief improvement consists in the use of carbonic acid as free as possible from oxygen. The carbonic acid generator is formed of two vessels. The lower one consists of a bottle with a tubular in the side near the bottom; this bottle is supported in an inverted position, and contains the marble from which the gas is generated. The upper vessel consists of a similar bottle standing upright; this con-

tains the hydrochloric acid required to act on the marble. The two vessels are connected by a glass tube passing from the side tubular of the upper vessel to the inverted mouth of the lower vessel; the acid from the upper vessel thus enters below the marble. Carbonic acid is generated and removed at pleasure by opening a stop-cock attached to the side tubular of the lower vessel, thus allowing hydrochloric acid to descend and come in contact with the marble. The fragments of marble used have been previously boiled in water. The boiling is conducted in a strong flask. After boiling has proceeded some time, a caoutchouc stopper is fixed in the neck of the flask, and the flame removed; boiling will then continue for some time in a partial vacuum. The lower reservoir is nearly filled with the boiled marble thus prepared. The hydrochloric acid has been also well boiled, and before it is introduced into the upper reservoir it has dissolved in it a moderate quantity of cuprous chloride. As soon as the acid has been placed in the upper reservoir it is covered by a layer of oil. The apparatus being thus charged is at once set in active work by opening the stop-cock of the marble reservoir; the acid descends, enters the marble reservoir, and the carbonic acid produced drives out the air which is necessarily present at starting. As the acid reservoir is kept on a higher level than the marble reservoir, the latter is always under internal pressure, and leakage of air from without cannot occur.

The presence of the cuprous chloride in the hydrochloric acid not only ensures the removal of dissolved oxygen, but affords an indication to the eye of the maintenance of this condition. So long as the acid remains of an olive tint, oxygen will be absent; but should the acid become of a clear blue-green, it is no longer certainly free from oxygen, and more cuprous chloride must be added.

A further slight improvement adopted since the last communication consists in the use of freshly-boiled reagents, which are employed in as small a quantity as possible. When boiling the hydrochloric acid it is well to add a few drops of ferrous chloride, in order more certainly to remove any dissolved oxygen.

The mode of operation is as follows:—The apparatus previously described is fitted together, the long funnel tube attached to the bulb retort being filled with water. Connection is made with the glass stop-cock of the carbonic acid generator by means of a short stout caoutchouc tube, provided with a pinch-cock. The pinch-cock being opened, the stop-cock is turned till a moderate stream of bubbles rises in the mercury trough; the stop-cock is left in this position, and the admission of gas is afterwards controlled by the pinch-cock, pressure on which allows a few bubbles to pass at a time. The heated chloride of calcium bath is next raised, so that the bulb retort is almost submerged; the temperature, shown by a thermometer which forms part

of the apparatus, should be 130° — 140° . By boiling small quantities of water or hydrochloric acid in the bulb retort in a stream of carbonic acid the air present is expelled; the supply of carbonic acid must be stopped before the boiling has ceased, so as to leave little of this gas in the retort. Previous to very delicate experiments it is advisable to introduce through the funnel tube a small quantity of nitre, ferrous chloride, and hydrochloric acid, rinsing the tube with the latter reagent; any trace of oxygen remaining in the apparatus is then consumed by the nitric oxide formed, and after boiling to dryness, and driving out the nitric oxide with carbonic acid, the apparatus is in a perfect condition for a quantitative experiment.

Soil extracts may be used without other preparation than concentration. Vegetable juices, which coagulate when heated, require to be boiled and filtered, or else evaporated to a thin syrup, treated with alcohol and filtered. A clear solution being thus obtained, it is concentrated over a water-bath to the smallest volume, in a beaker of smallest size. As soon as cool, it is mixed with 1 c.c. of a cold saturated solution of ferrous chloride and 1 c.c. of hydrochloric acid, both reagents having been boiled and cooled immediately before use. In mixing with the reagents care must be taken that bubbles of air are not entangled; this is especially apt to occur with viscid extracts. The quantity of ferrous chloride mentioned is amply sufficient for most soil extracts, but it is well perhaps to use 2 c.c. in the first experiment of a series; the presence of a considerable excess of ferrous chloride in the retort is thus ensured. With bulky vegetable extracts more ferrous chloride should be employed; to the syrup from 20 grams of mangel sap I have usually added 5 c.c. of ferrous chloride, and 2 c.c. of hydrochloric acid.

The mixture of the extract with ferrous chloride and hydrochloric acid is introduced through the funnel tube, and rinsed in with three or four successive half cubic centimeters of hydrochloric acid. The contents of the retort is then boiled to dryness, a little carbonic acid being from time to time admitted, and a more considerable quantity used at the end to expel any remaining nitric oxide. The most convenient temperature is 140° , but in the case of vegetable extracts it is well to commence at 130° , as there is some risk of the contents of the retort frothing over. The gas is collected in a small jar over mercury. As soon as one operation is completed, the jar is replaced by another full of mercury, and the apparatus is ready to receive a fresh extract. A series of five determinations, with all the accompanying gas analyses, may be readily performed in one day. The bulb retort becomes encrusted with charcoal when extracts rich in organic matter are the subject of analysis; it is best cleaned first with water, and then by heating oil of vitriol in it.

Mercury, contrary to the statement in most text-books, is gradually attacked by hydrochloric acid in the presence of air; the mercury in the trough is thus apt to become covered with a grey chloride, and it is quite necessary to keep the store of mercury in contact with sulphuric acid to preserve its mobile condition.

The gas analysis is of a simple character; the gas is measured after absorption of the carbonic acid by potash, and again after absorption of the nitric oxide, the difference giving the amount of this gas. For the absorption of nitric oxide, a saturated solution of ferrous chloride was for some time employed. This method is not, however, perfectly satisfactory when the highest accuracy is required, the nitric oxide being generally rather underestimated, except the process of absorption is repeated with a fresh portion of ferrous chloride. The error is greater in proportion to the quantity of unabsorbed gas present. Thus, with a mixture of nitrogen and nitric oxide containing little of the former, absorption of the nitric oxide by successive treatment with oxygen and pyrogallol over potash showed 97·8 per cent. of nitric oxide; while the same gas, analysed by a single absorption with ferrous chloride (after potash), showed 97·5 per cent. of nitric oxide. With a mixture containing more nitrogen, the oxygen method showed 65·9 per cent. of nitric oxide; while one absorption with ferrous chloride gave 64·2 per cent., and a second absorption, in which the ferrous chloride was plainly discoloured, 66·2 per cent. The use of ferrous chloride as an absorbent for nitric oxide has now been given up, and the oxygen method substituted. All the measurements of the gas are now made without shifting the laboratory vessel; the conditions are thus favourable to extreme accuracy.

The chief source of error attending the oxygen process lies in the small quantity of carbonic oxide produced during the absorption with pyrogallol; this error becomes negligible if the oxygen is only used in small excess. The difficulty of using the oxygen in nicely regulated quantity may be removed by the use of Professor G. Bischof's recently-invented "gas delivery-tube." This may be made of a test-tube, having a small perforation half an inch from the mouth. The tube is partly filled with oxygen over mercury, and its mouth is then closed by a finely-perforated stopper, made from a piece of wide tube, and fitted tightly into the test-tube by means of a covering of caoutchouc. When this tube is inclined, the side perforation being downwards, the oxygen is discharged in small bubbles from the perforated stopper, while mercury enters through the side opening. Using this tube, the supply of oxygen is perfectly under control, and can be stopped as soon as a fresh bubble ceases to produce a red tinge in the laboratory vessel. The trials made with this apparatus have been very satisfactory.

In the following table will be found a number of test experiments made with nitrate of potassium by the method just described. The gases were analysed the same day in which they were obtained, save in the case of Experiments 3 and 7, in which the analysis was made on the following day.

In Experiments 3, 4, and 7, the nitric oxide was absorbed by ferrous chloride; in all other cases the oxygen method was employed. The gas found in each stage of the analysis is for convenience reckoned as nitric oxide, and expressed in milligrams of nitrogen.

Test Experiments with known quantities of Nitre, conducted in an Atmosphere of Carbonic Acid free from Oxygen.

No.	Nitrogen taken as nitre, milligrams.	Gas obtained expressed as milligrams of nitrogen.			Nitrogen found as nitric oxide for 100 taken.
		Total gas after potash.	Nitric oxide absorbed.	Gas left unabsorbed.	
1	5.092	5.080	5.042	0.038	99.0
2	5.092	5.050	5.023	0.027	98.6
3	2.828	2.824	2.790	0.034	98.7
4	2.828	2.774	2.746	0.028	97.1
5	2.560	2.522	2.505	0.017	97.9
6	2.560	2.585	2.563	0.022	100.1
7	1.414	1.411	1.361	0.030	97.7
8	1.023	1.040	0.992	0.048	97.1
9	1.019	1.081	1.003	0.078	98.4
10	1.019	1.081	0.985	0.046	96.7
11	0.512	0.539	0.516	0.023	100.8
12	0.505	0.519	0.496	0.023*	98.2

The figures show that the modifications introduced have issued in a considerable improvement in the result, the small quantities of nitrogen taken having yielded an average product of 98.4 per cent. This favourable product does not show any diminution even when only half a milligram of nitrogen is the subject of experiment. In Experiment 9 0.2 gram of cane-sugar was added with the nitre, but without affecting the result.

We have thus in the reaction proposed by Schloesing a means of determining very small quantities of nitric acid with considerable accuracy, even in the presence of organic matter; but to accomplish this, the various simplifications, consisting in the omission of the stream of carbonic acid, and the collection of the gas over caustic soda, must be abandoned, and special precautions must be taken to exclude all trace of oxygen from the apparatus.

* The unabsorbed gas was lost in this experiment; it is reckoned as the same as that found in the duplicate experiment, No. 11.

LV.—*On the Determination of Nitric Acid in Soils.*

By ROBERT WARINGTON.

As the nitrogen contained in cereal, and in many other crops, is at least in greatest part derived from the nitrates of the soil, the quantity of nitrates present in a soil becomes for many purposes a measure of the assimilable nitrogen which the soil contains. Investigations as to the increase or diminution of the nitrates of the soil under various circumstances of manuring, culture, or season, have been for some time past in progress at Rothamsted. As a part of this work, attention has naturally been directed to perfecting the methods employed for determining nitrates in soil. Some results of the experience thus acquired it is proposed to lay before the Society.

1. *Collection of the Soil Samples.*

A fair sample of soil is best taken by driving into the ground a short iron tube, of the depth which it is desired the sample shall represent. When the upper edge of the tube is level with the surface of the ground, the soil filling the tube is cut out, and constitutes the sample. If a sample of the second depth is desired, the earth surrounding the tube is cleared away, and the tube is once more driven down, till its upper edge is at the level which the lower edge previously occupied. By proceeding in this way the soil may be sampled to any required depth. The iron tube should be wide enough to prevent any abnormal consolidation of the soil within it, else the length of the tube will not exactly represent the depth of soil taken. The method here indicated has been employed by Messrs. Lawes and Gilbert during the last 25 years; the tubes made use of are rectangular, and 9 inches deep; the smallest is 6 inches square.

In sampling a soil for nitrates it is advisable to extend the collection to a considerable depth, as although nitrates are formed at the surface, they are readily washed down by rain, and distributed by diffusion; the whole range of soil available to the roots should therefore, if possible, be included. If only a comparatively small depth of soil can be sampled, it is very necessary that the sampling should be done after dry weather, when the nitrates are nearest the surface.

2. *Treatment of the Soil Samples.*

The first step to be taken is to bring the soil as quickly as possible to a dry condition. If this is not done, the quantity of nitric acid

found may greatly exceed that existing in the original soil, as nitrification will be continually in progress while the soil remains damp.

Experience has shown that it is not unimportant at what temperature the drying is effected. If a wet soil is dried in a water-oven at a temperature approaching 100° , the nitrates present will be more or less destroyed. This destruction is probably due to deoxidation by the organic matter present, and will be in proportion to the mass of the soil, its wetness, and its richness in organic matter. While, however, drying in a water-oven occasions loss of nitrates, drying by mere exposure to air is equally likely (in the case of surface soils at least) to occasion a gain in nitrates, the drying being so slow that a sensible amount of nitrification may occur.

The following test experiments have been made to ascertain the influence of various modes of drying:—An arable loam*, representing the first 9 inches from the surface, was passed through a sieve with meshes half an inch diameter, to separate stones; the sifted soil weighed about 280 lbs. The fine mould of this soil contained about 18 per cent. of water. The soil was well mixed, and divided into several portions. One-eighth was dried in the water-oven for 24 hours at about 90° ; one-eighth was dried in the stove room at 38° ; one-eighth was dried by exposure to air during 17 days, at a mean temperature of 10.2° ; one-half was placed in a bag, and kept in an outer shed during seven months (October to April). The whole of the samples were finally powdered and sifted, and all visible roots removed. The nitrogen existing as nitric acid was then determined in all the samples by the Crum-Frankland method. About four years afterwards the determinations were repeated, using the modification of Schloesing's method now adopted for soil analysis; the results are given in Table I.

TABLE I.—*Variations in the Quantity of Nitrates present in Soil resulting from Different Modes of Drying.*

Treatment of soil.	Analysed 1878.		Analysed 1882.	
	Water.	Nitrogen as nitrates in dry soil, Crum-Frankland method.	Water.	Nitrogen as nitrates in dry soil, Schloesing method.
	p. c.	per million.	p. c.	per million.
1. Dried in water-oven, 90°	0.99	1.08	1.57	4.17
2. Dried in stove, 38°	2.13	4.88	2.22	5.64
3. Dried in air, 10°	3.53	6.04	3.12	6.77
4. Kept in bulk 7 months, then dried in air	4.22	8.90	3.62	9.18

* The Rothamsted soil, to which all the experiments here quoted refer, may be described as a heavy loam with a clay subsoil.

The analyses made by the Crum-Frankland method show a wide range of variation in the quantity of nitric acid found, the amount being least when the soil was dried in the water-oven, and most when the soil had been left in bulk for several months and was finally sifted and powdered without the use of artificial heat. The later analyses of the same series of soils by the Schloesing method show much less variation in the contents of nitric acid, but the differences all lie in the same direction as before. The want of agreement in the two series is principally due to the much greater amount of nitric acid found by Schloesing's method in the case of the soil dried in the water-oven; we shall see presently that this higher result is probably more correct than that shown by the Crum-Frankland process.

We shall probably have no difficulty in concluding that the quantity of nitric acid found in the soils numbered 3 and 4 is in excess of that originally present, the process of drying in these cases having afforded more or less opportunity for nitrification; but the facts before us do not prove that the nitrates found after drying in the water-oven were too low. The following experiments supplement those just quoted, and show the influence of heat and moisture in diminishing the amount of nitrates in a soil.

In a dry powdered sample of arable soil, representing the first 9 inches from the surface, nitric acid was in the first place determined. Three quantities of this soil were then taken, each of 300 grams. One lot was treated with 60 c.c. of water free from ammonia, the water being carefully added so as not to destroy the open texture of the soil; the moistened soil was then made into a cubical mass, and placed in the middle of a basin. The second lot was similarly treated, placed loosely in a beaker, which it nearly filled, and covered with a clock-glass. The third lot was gradually introduced into a similar beaker containing 130 c.c. of water; the soil in falling through the water parted with most of its air; the water was sufficient to slightly cover the mass of soil. This beaker was also covered by a clock-glass. The three soils were then placed in a large water-oven for about 24 hours; the water was in actual ebullition during eight hours. The quantities of nitric acid found before and after this treatment were as follows; the analyses were all made by Schloesing's process:—

TABLE II.—*Influence of Heat and Moisture in reducing the Nitrates present in Soil.*

Treatment of soil.	Nitrogen as nitrates per million of soil.
1. Original soil	8.08
2. Ditto, moistened, and quickly dried in water-oven	7.78
3. Ditto, moistened, and slowly dried in water-oven.....	6.34
4. Ditto, thoroughly wetted, and heated in water-oven	1.83

It appears from these figures that with the particular soil in question little error was introduced by heating in the water-oven, if only drying was quickly effected; but where, as in Experiment 3, the escape of water was hindered, a very distinct reduction of nitrates took place. The fourth experiment proves that in the case of a mass of soil saturated with water, a comparatively short exposure to a high temperature is sufficient to destroy most of the nitric acid present. Other experiments made at Rothamsted (*Jour. Roy. Agri. Soc.*, 1881, 332) have shown that a soil kept saturated with water will lose nitrates even at ordinary temperatures, and similar facts have been noticed by Schloesing and others.

As drying wet soil at a high temperature thus tends to a loss of nitrates, while slow drying at low temperature admits, on the other hand, of their production, the following course has been adopted at Rothamsted:—The soil is broken up immediately it is received from the field, and spread in trays, in layers about 1 inch in thickness; the trays are then placed in a stove room, kept at about 55°; the drying is usually completed in 24 hours. As the temperature of the room is one at which nitrification by an organised ferment does not occur, it is probable that very little production of nitric acid takes place during the operation. After drying, stones and roots are removed, and the soil is finely powdered and placed in bottles. Soil samples thus prepared are not absolutely dry, but the small amount of water present is apparently insufficient to allow of organic change.

3. *Preparation of a Watery Extract.*

The mode of extracting the nitrates employed by Boussingault, and still recommended in works on agricultural analysis, is to take 500—1000 grams of the soil, add its own weight of water (twice its weight is recommended by Wolff), and shake thoroughly; after standing, a portion of the fluid is removed for analysis. This mode of proceeding

demands a considerable amount of soil, the extraction occupies a good deal of time, and the extract obtained is weak and turbid. Moreover some amount of uncertainty will generally attach to the calculated relation between the weight of soil taken and the nitric acid found; for if the soil is moist it will be difficult to decide how much of this moisture is diffusible water, and how much exists as hydrates; while if the soil has been dried at 100°, a part of the water added will doubtless combine with the soil, and cease to form part of the solution.

Grandean (*Traité d'Analyse des Matières Agricoles*, 1877, 157) has proposed to extract the nitrates by simple percolation; but as, according to his directions, four hours are required to extract 50 grams of soil, while the resulting extract measures 150 c.c., the advantages offered seem very small.

The method now employed at Rothamsted is to extract the soil by percolation on a vacuum filter. A funnel $4\frac{1}{2}$ inches wide is made by cutting off the top of a Winchester quart bottle; at the bottom of this funnel a disc of copper gauze is laid, and on this two discs of filter-paper, each slightly wider than the one beneath. The filter is first moistened, and the dry powdered soil is then introduced; 200—500 grams are usually taken, according to the supposed richness of the soil in nitrates. If the soil is of loose texture, it is shaken firmly together, but with a clay soil consolidation is better avoided. The funnel is now connected by a caoutchouc stopper and glass tube, with a strong flask, water is poured on the soil, and the flask is put in connection with a water-pump. The water descends through the soil, and is collected in the flask. When 100 c.c. have passed through, it may be concluded that all nitrates have been extracted. The collection of this extract may take from 10 minutes, in the case of a surface soil of loose texture, to 45 minutes in the case of a subsoil. The extract is nearly clear. Second extracts have frequently been taken, but no chlorides or nitrates have been found in them.

The small volume of the extract in which all the chlorides and nitrates of a soil may be obtained, if the soil is taken dry, and percolation is conducted on a vacuum filter, is truly astonishing. In an experiment already published (*Jour. Roy. Agri. Soc.*, 1881, 329), 7 lbs. of dry powdered soil were placed on a filter, similar to that just described, the soil forming a column 8 inches in height; the filter was then put in connection with the pump, and water applied to the surface of the soil. In $2\frac{1}{4}$ hours the water had descended through the column of soil, and percolation commenced. It was found that the first 50 c.c. of extract contained more than three-quarters of the chlorides and nitrates present in the soil, while in the first 150 c.c. the whole of the chlorides, and 98.8 per cent. of the nitrates were found. It would

appear that as a column of water descends through a dry powdered soil, it dissolves the soluble salts at its lower edge, and pushes this solution before it till the area of discharge is reached. If the soil were wet instead of dry, a much larger extract would be required to obtain all the chlorides and nitrates, as it would then be necessary to displace all the water present in the soil.

4. *Analysis of the Soil Extract.*

The watery extract obtained by the method just described is placed in a small basin, and evaporated nearly to dryness on a water-bath. The extract is usually acid to litmus, and when highly concentrated may be strongly so. I have usually made the solution slightly alkaline with lime-water before evaporation, but some test experiments with and without lime-water have not shown that this treatment is of any importance. The extract from an arable soil yields, when concentrated, a very small quantity of pale-brown syrupy liquid; a pasture soil, being much richer in organic matter, yields a much more considerable extract.

The extract from a soil which has been dried at a high temperature is much richer in organic matter, and apparently also in some saline constituents, than the extract from the same soil dried at a low temperature. Thus the extract (100 c.c.) from 300 grams of the soil dried in the water-oven (Experiment 1, Table I), gave a dry residue of 0.239 gram, while similarly prepared extracts from the soils dried at 10° and at 38°, gave only 0.107 and 0.104 gram, of solid matter. The temperature at which a sample of soil is dried thus considerably affects other ingredients besides the nitrates.

Two methods have been employed at Rothamsted in recent years for determining the quantity of nitric acid in soil extracts. The earlier determinations were made by the well known Crum-Frankland method, in which the concentrated fluid is introduced into a tube of special construction, mixed with $1\frac{1}{2}$ times its volume of concentrated sulphuric acid, and shaken with mercury; the resulting nitric oxide gas being then measured. Test experiments made with this method have been already communicated to the Society (*Trans. Chem. Soc.*, 1879, 375).

In applying this method to the analysis of soil extracts, it was soon found that the amount of soluble organic matter present was far too great, at least in the case of extracts from surface soils, for its convenient or accurate use; much froth was produced in the shaking tube, and the results obtained were proved to be below the truth. The effect of organic matter in diminishing the amount of nitric oxide obtained has been already pointed out in the communication just referred to.

Further experiments with soil extracts showed, however, that the greater part of the organic matter could be removed by treatment with alcohol. The mode of operation was to concentrate the watery extract from the soil to a small bulk, then add several times its volume of strong spirit, and filter. The bulky precipitate was well washed with spirit, and the filtrate and washings evaporated to dryness. The residue left had the appearance of a thin varnish; this was dissolved in a few drops of water and introduced into the shaking tube.

A later improvement consisted in the introduction of a single drop of dilute hydrochloric acid into the shaking tube before commencing the agitation; by this means the attack on the mercury is much intensified, and the evil influence of organic matter diminished. When using this small quantity of hydrochloric acid, no instance has occurred of a subsequent development of gas in the laboratory vessel of the gas analysis apparatus due to an incomplete reaction in the shaking tube.

To ascertain whether the organic matter in a purified soil extract had any influence on the result, test experiments were made. Extracts were prepared in the usual way from a pasture soil proved to contain no nitrates; to each of these extracts 10 c.c. of a solution of nitre were added; the extracts were then concentrated, purified with alcohol, and analysed with the addition of hydrochloric acid. In some cases the

TABLE III.—*Determinations of Nitric Acid by the Crum-Frankland Method. Nitre Solutions alone, and mixed with Soil Extracts.*

	Nitrogen found. Total gas reckoned as nitric oxide.
<hr/>	
10 c.c. Normal Nitre Solution.	milligrams.
1. Nitre only	1·362
2. Ditto	1·369
3. Ditto	1·370
4. Nitre evaporated with 1st extract from soil	1·354
5. „ added to alcohol extract	1·447
6. „ evaporated with 1st extract from soil	1·593
7. „ added to alcohol extract	1·569
8. „ evaporated with 2nd extract from soil	1·263
9. Ditto ditto	1·279
10. Ditto ditto	1·297
11. Nitre added to alcohol extract	1·330
10 c.c. $\frac{1}{4}$ Nitre Solution.	
12. Nitre evaporated with 2nd extract from soil.....	0·166
13. „ added to alcohol extract	0·234
10 c.c. $\frac{1}{8}$ Nitre Solution.	
14. Nitre added to alcohol extract.....	0·037

nitre was not evaporated with the original extract, but added to the residue left on evaporating the alcohol extract, any possible reduction of nitrates during the evaporation, or loss during treatment with alcohol, was thus avoided. In several of the experiments a second extract from the soil was made use of. The results will be found in Table III.

The normal nitre solution employed contained in 10 c.c. 1.388 mgrms. of nitrogen.

In the above results the whole of the gas obtained on shaking with mercury has been reckoned as nitric oxide; this, however, is not absolutely the case. When using the Crum-Frankland method in the presence of organic matter, any gas produced before shaking with mercury cannot safely be removed from the tube, as this gas may consist in great part of nitric oxide (*Trans. Chem. Soc.*, 1879, 383); indeed, in some soil extracts, rich in organic matter, two-thirds of the whole gas has been evolved before shaking. That some gas other than nitric oxide was produced, was proved on several occasions. Thus a soil extract precisely similar to that employed in Experiments 4 and 5, but without nitre, when shaken with sulphuric acid yielded gas which would have been reckoned as 0.051 mgrm. of nitrogen. Of the large gas obtained in Experiment 6, 0.257 mgrm. was found to be unabsorbed by ferrous chloride. There is no doubt therefore that the quantities of nitrogen calculated from the volumes of the gas are rather higher than those actually obtained.

In the experiments in which 10 c.c. of normal nitre solution were added to the soil extract, the nitrogen introduced was on the whole fairly recovered on analysis. The results are not nearly so good when we turn to the smaller quantities of nitre. In Experiment 13 about two-thirds of the nitrogen added is recovered on analysis, and in Experiment 14 less than one quarter; in both these experiments the reaction was pushed as far as possible, the solutions being heated in the shaking tube and reshaken. In the earlier investigation of the Crum-Frankland method, already referred to, the same fact appeared; a small quantity of nitric acid suffering a greater absolute loss from the presence of sugar than a large quantity. When applying the method to actual soil analysis, the same truth is manifest, an increase in the quantity of soil taken producing an increase in the percentage of nitric acid found when the soil is poor in nitrates.

The Crum-Frankland method having proved only partially satisfactory, trials were made with the method recommended by Schloesing for the determination of nitrates in organic extracts, namely, heating with ferrous chloride and hydrochloric acid, and collection of the nitric oxide evolved. A general investigation of this method has been already published (*Trans. Chem. Soc.*, 1880, 468); a description of

improvements recently adopted will be found in the present volume, pp. 345—350. The method has been found to yield excellent results in the presence of organic matter. With this method a few test-experiments with soil extracts have been made, the same soil being used as in the preceding series. The extracts were used without purification with alcohol. The results will be found in Table IV.

TABLE IV.—*Determinations of Nitric Acid by Schloesing's Method. Nitre Solutions alone, and mixed with Soil Extracts.*

	Nitrogen found as nitric oxide.
	milligrams.
1. Nitre only.....	2·713
2. „ evaporated with 1st extract from soil	2·699
3. „ added to extract after evaporation.....	2·691
4. „ only.....	1·325
5. „ evaporated with 1st extract from soil	1·325
6. Ditto ditto	1·376

The quantity of nitre solution employed in Experiments 4 to 6, was rather less than that used in the experiments quoted in Table III.

The results obtained are seen to be quite satisfactory, the known quantity of nitrate added being fully recovered on analysis; the organic matter present in the soil extract is, apparently, with this method entirely without effect on the result.

As the organic matter of soil has no influence, when the analysis is made by Schloesing's method, while it lowers the result, even after treatment with alcohol, when the Crum-Frankland method is employed, it follows that the same soil analysed by these two methods will give somewhat higher results by the former than by the latter; this has uniformly proved to be the case when duplicate determinations have been made. This fact will serve to explain the discrepant results found in Table I.

We have apparently in Schloesing's method a really satisfactory means of determining nitrates in soil. The soil extract requires in this case no preliminary purification, but may be analysed as soon as concentrated. The method is equally capable of determining large or small quantities of nitric acid, while the amount of nitric oxide produced is ascertained with the greatest precision by gas analysis. Full details respecting the conduct of this method will be found in the papers above referred to.

The indigo method for determining nitric acid is quite unsuitable for soil analysis. In an earlier communication (*Trans. Chem. Soc.*, 1879,

588) some comparative determinations by the indigo and Crum-Frankland methods were given; I may here add a few comparative determinations by the indigo and Schloesing methods of the nitrates in an arable soil, showing that the indigo method fails even in the analysis of the extract from a clay subsoil. The figures represent the nitrogen existing as nitrates per million of soil.

	Schloesing's method.	Indigo method.
First 9 inches from surface.....	8.08	5.18
Second " " ".....	4.98	3.78
Third " " ".....	2.66	2.03

The nitric acid shown by indigo is in the first 9 inches 64.1 per cent., in the second 9 inches 75.9 per cent., and in the third 9 inches 76.3 per cent. of the truth, the result improving somewhat as the amount of organic matter diminishes.

LVI.—COMMUNICATIONS FROM THE LABORATORY OF THE UNIVERSITY OF TOKIO, JAPAN.

Metallic Compounds containing Bivalent Hydrocarbon Radicals. Part III.

By J. SAKURAI, F.C.S.

WHEN monomeric methylene iodide (see this Journal, 1880, Trans., 658) and mercuric chloride were mixed together, and the mixture was covered with alcohol, a reaction took place after some time, whereby another new organometallic compound of the class under consideration was formed.

In order to obtain this body quickly, and in a state of purity, the following plan was adopted:—

Monomeric methylene iodide was mixed with mercuric chloride in the proportion of 468 ($= \text{CH}_2\text{HgI}_2$) to 271 ($= \text{HgCl}_2$) parts by weight, and both in a state of fine powder, and the mixture was cohobated with alcohol for an hour, in a flask fitted with an upright condenser. On cooling, the alcoholic solution deposited a considerable quantity of a white shining crystalline substance. On addition of water to the contents of the flask, a further deposition of the crystals took place, together with mercuric iodide. They were washed with water till free from mercuric chloride, then digested with a strong

solution of potassic iodide in order to dissolve out the mercuric iodide, and finally washed with water till the washings showed no turbidity with nitrate of silver. The residue was dried first between blotting-paper, and then over sulphuric acid. When dry, it was digested with hot ether, and the ethereal solution, on spontaneous evaporation, left behind a mass of substance, beautifully crystallised in thin shining plates of silk-white colour, and having a slight mercurial odour, common to the organometallic compounds. The presence in it of mercury, iodine, and chlorine, as well as of carbon, was distinctly indicated by the ordinary methods.

The compound is soluble in ether, chloroform, and alcohol, but quite insoluble in water. It melts at 129° , yielding, on cooling, a slightly yellowish mass, which remelts at the original temperature. Heated with a solution of iodine in potassic iodide, it yields an oily liquid, having a sweetish smell, like that of chloroform.

As in the analyses of the other organometallic bodies described in previous papers, the amount of iodine needed for the decomposition of this compound was determined by a standard solution of sodic thiosulphate, and the mercury as sulphide. The results are recorded below :—

	I.	II.
Substance taken	0.152000	0.17400
Iodine taken	0.278500	0.30510
„ left	0.176088	0.18582
„ needed.....	0.102412	0.11928
Also mercuric sulphide ..	—	0.10800

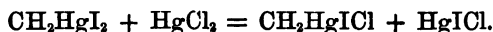
From these numbers it appears that the amount of iodine needed for the decomposition of 100 parts of the compound, and the quantity of mercury therein contained are as follows :—

	I.	II.	Mean.
Iodine needed	67.37	67.356	67.363
Mercury.....	—	53.500	53.500

These numbers agree with those calculated for the formula CH_2HgICl , viz. :—

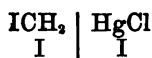
Iodine needed	67.46
Mercury	53.12

From the mode of its preparation, as well as from the analytical results, there is no doubt that the new compound is *monomeric methylene chloriodide*, and formed in the following way :—

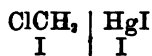


Now, since monomeric methylene iodide was proved to have

the formula $I(CH_2)HgI$, a question naturally arises as to which of the iodine-atoms is replaced by chlorine in the new compound. This question was answered by the facts derived from the study of the reaction which the compound undergoes with iodine. If it is to be represented by the formula $I(CH_2)HgCl$, then iodine would decompose it into methylene iodide and mercuric chloride, thus—



If, on the other hand, it has the constitution $Cl(CH_2)HgI$, then the action of iodine upon it would be to produce methylene chloriodide and mercuric iodide, thus:—



The oily liquid, before mentioned as the product of the action of iodine upon monomeric methylene chloriodide, was found, on purification, to contain both iodine and chlorine. It boils at 129° , and has a density of 2.49 at 20° . A determination of iodine and chlorine in it was made with the following results:—

556 gram of the liquid was decomposed by nitric acid and silver nitrate in a sealed tube; the resulting mixture of silver iodide and chloride weighed 1.202 grams. The whole of the silver was then reduced to the metallic state by nascent hydrogen, dissolved in nitric acid, and precipitated as chloride, which weighed .921 gram.

From these data the amounts of iodine and chlorine were calculated as follows:—

Iodine.	Chlorine.
70.15	21.30

On account of the number of operations which the analytical process involved, and of the indirect ways in which the determinations had to be made, a little discrepancy between the above figures and those calculated for methylene chloriodide which follow, may perhaps be overlooked without fear of serious error.

	Iodine.	Chlorine.
CH_2ICl	71.95	20.11

Methylene chloriodide has now, I believe, been obtained and described for the first time. Its physical properties are such as might be inferred from the close analogy between iodine and chlorine. Its boiling point, for instance, is very nearly the mean of the boiling points of methylene iodide and methylene chloride:—

Methylene iodide	$181^\circ C.$
„ chloriodide	109
„ chloride	40

Having established the fact that the above oily liquid is methylene chloriodide, we now come to the conclusion that monomeric methylene chloriodide has the latter of the two formulæ previously mentioned, viz., $\text{Cl}(\text{CH}_2)\text{HgI}$.

LVII.—*Some Observations on the Luminous Incomplete Combustion of Ether and other Organic Bodies.*

By W. H. PERKIN, F.R.S.

WHEN evaporating ether in a shallow vessel on a somewhat strongly heated sand-bath, it is always observed that vapours, irritating to the eyes, are formed. Some time since, when conducting an operation of this kind, in the evening when it was nearly dark, a pale blue flame was seen floating about on the surface of the sand, and yet not igniting the ether which was being evaporated. The experiment was repeated several times, and always with the same result. This phenomenon, which appears to have been almost lost sight of, has been previously observed. It was first noticed by Sir Humphry Davy (*Gmelin's Handbook of Chemistry*, 8, 179—180), who found that, when a hot spirally wound platinum wire was introduced into a mixture of ether vapour and air, it became red-hot, and in a dark room a pale phosphorescent light was observed above the wire, especially when it ceased to glow. Doebereiner noticed the same thing, but states that the blue lambent flame ceased when the platinum became red-hot. He also remarks that when ether is dropped into a retort heated on the sand-bath to 100° and upwards, or into a platinum capsule exposed to the vapour of boiling water, Leidenfrost's phenomenon (the spheroidal state) is produced, accompanied by a blue flame, visible only in the dark, and not capable of setting fire to other bodies, tear-exciting vapours of lampic acid being formed. As will be seen further on, the temperature of 100° , mentioned by Doebereiner, is insufficient to produce the blue flame. Boutigny, in 1837, observed that this phenomenon took place equally in a metal or porcelain dish, heated to a temperature a little below that of fusing lead, or about 260° , lampic acid being formed at the same time. Miller also mentions that the glowing extremity of a glass rod or piece of porcelain held over ether, exhibits a small blue flame and forms a large quantity of acid.

Although the foregoing facts are known, it was thought that it would be interesting to make a few more experiments on this remark-

able kind of combustion, and to see if other bodies besides ether were capable of producing the same effect.

The temperature at which ether begins to burn with this blue flame is about 260° , and any temperature between that and a dull red heat may be used. The higher the temperature, however, the more likely is ordinary combustion to set in.

There are several ways by which this phenomenon may be produced on a sufficiently large scale to exhibit at lectures. The most simple way is to project ether from a wash-bottle on to a thick iron plate heated nearly to dull redness; but it is better to use a thick iron dish heated over a Bunsen burner, and after the gas has been turned off, or the lamp so screened that no light escapes into the room, to make the jet of ether play on various parts of the surface; in this way a considerable mass of blue flame may be obtained. The best way of showing this flame, however, is to take a copper or iron ball, about 2 or 3 inches in diameter, provided with an eye, so that it may be suspended from a wire, heat it to dull redness, and as soon as it has cooled, so as to be nearly invisible in the dark, place it over a dish about 4 inches in diameter, containing several filter-papers well drenched with ether. As the ball approaches the ether, a beautiful blue flame will form, passing over its heated surface upwards for several inches. The ball may be let right down into the ether without causing ordinary combustion.

This peculiar combustion of ether may also be shown in a glass tube. A large tube is taken, about 4 cm. in diameter, 60 or 70 cm. long, bent at right angles about 15 cm. from the end, this is fixed, with the bend downwards, in a clamp, and some ether poured into it, but not sufficient to prevent a free current of air from passing through the tube. On heating the longer arm of the tube with a Bunsen burner, a draught is instituted, and when the walls of the tube are sufficiently heated, a blue light will be seen on putting out the lamp. If the tube be now shaken to increase the volatilisation of the ether, a blue flame will fill the arm of the tube, and issue out into the air. It then often enters into ordinary combustion at the opening, and the peculiar effect of the combustion of ether in two manners may be seen at the same time; the blue flame inside the tube, is, however, much masked by the luminosity of that outside. The experiment soon afterwards comes to an end by the ordinary flame passing down to the ether, when it is necessary to close the tube to extinguish it.

This blue flame from ether has a comparatively low temperature. The fingers may be placed in it with impunity. It will not char paper or ignite carbon disulphide, and a lucifer match held in it at first becomes only phosphorescent, and is some time before it is ignited. Ether vapour burning with this blue flame, when in large quantities,

or more especially when in a confined space, rapidly increases in temperature and quickly enters into ordinary combustion.

As it appeared from some small experiments that this kind of combustion was attended with the production of but small quantities of carbonic anhydride, a quantitative experiment was made to settle this point.

The arrangement was as follows:—A Woulff's bottle containing ether was provided with a tube opening under the liquid, so that when air was aspirated through it, it would be saturated with the ether vapour. This was connected by ordinary quill-tubing with a piece of combustion-tube about 20 cm. long, laid in a thick metal trough, and heated with a Bunsen burner. Connected with this by means of a tube bent at right angles, was a large test-tube, cooled in a freezing mixture of ice and salt, to condense ether and other products. To this was attached a Liebig's bulb full of concentrated sulphuric acid, to absorb any uncondensed vapour of ether and other bodies, and then a weighed potash apparatus for the absorption of carbonic anhydride. Lastly, this was connected with an aspirator of known capacity.

On drawing air through the ether, the blue flame formed in the heated piece of combustion-tube, and travelled backwards and forwards, but never passed from it. After the operation had gone on until several litres of air had been aspirated, it was stopped, the potash-bulbs weighed, and the gas in the aspirator measured and analysed (it was nearly pure nitrogen). In this way it was found that the amount of oxygen consumed amounted to 1.313 gram, and the carbonic anhydride produced to only 0.133.

The liquid condensed in the test-tube in the freezing mixture was fractioned, and found to consist chiefly of aldehyde and ether: a small quantity of an oil boiling above 100° , and apparently crotonic aldehyde, was also present.

On making experiments with other bodies, it has been found that the luminous appearance accompanying incomplete combustion is not peculiar to ether, though, so far as observations have been made, it appears to be the best example we have. Acetic aldehyde is the next best, and gives a very beautiful blue flame when the vapour passes over a heated copper ball. The alcohols up to amyl give but traces of blue flame, methyl alcohol giving none. The following results were obtained with the hydrides:—Pentane gave a trace of flame; hexane, a considerably better result; heptane, a still greater improvement; and this increase was found to go on up to solid paraffin, which, when thrown on a heated surface or fused on a hot metallic ball, gives a good blue flame.

Benzene and its homologues give no result; neither do phenol and cresol.

With the fatty acids, no result is obtained with the two lower members of the series, but it begins with propionic acid, which gives a very small effect. Butyric acid acts, however, somewhat better. Stearic acid, when heated, becomes luminous at about 250° , and this increases gradually in intensity; with the temperature at 290° blue flames appear, and, when heated somewhat higher, the vapour enters into ordinary combustion.

Oleic acid behaves in the same way as stearic, becoming quite visibly luminous at $250\text{--}260^{\circ}$; blue flames form at 310° , after which it soon catches fire.

Benzoic, cinnamic, and phthalic acids give no result.

Olive and linseed oils, and white wax, behave like oleic acid when heated.

Spermaceti shows this effect very well, and is a very suitable substance for its exhibition at a lecture. It may be shown in two ways: first by throwing pieces on a strongly heated iron plate; these form luminous patches as they melt; but by far the best way is to bring it in contact with the upper side of a strongly heated metallic ball, suspended by a wire; then as it melts and flows over the ball, it produces a beautiful effect, the vapour evolved being also luminous. Spermaceti, when heated in a dish, becomes luminous, and this effect increases with the temperature; at 300° pale-blue flames flicker over its surface, and at about 360° it ignites. On cooling, the luminosity gradually decreases, and it is difficult to find the point at which it perfectly fades away, but it may be seen even as low as 130° . This is true of all the other bodies which have been tried in this manner.

It was thought of interest to see to what extent carbonic anhydride was given off from some of these bodies of high molecular weight when in a luminous state. Some solid paraffin was therefore taken for this purpose. It was heated in a retort up to about $160\text{--}170^{\circ}$, air being drawn through it; the products were freed from water and organic matter by passing through sulphuric acid, and then passed through potash to absorb the carbonic anhydride, the amount of air passed being calculated from that in the aspirator, which was analysed. The experiment showed that 0.3816 gram of oxygen had been used, and only 0.025 of CO_2 formed, a result similar to that which was obtained in the case of ether.

We thus see that with the paraffins, fatty acids, and probably alcohols, their power of producing this phenomenon increases with their molecular weight, and that bodies of the aromatic series do not possess this power.

The blue flames and the luminous appearance which result from imperfect combustion are no doubt similar to ordinary phosphorescence produced during the imperfect combustion of phosphorus, the only dif-

ference being that while these various substances require to be heated, phosphorus shows this phenomenon at ordinary temperatures.

The physical properties of the blue flame produced by different substances seem to be the same. The light is too feeble to examine in detail with the spectroscope; but no bands are seen.

LVIII.—CONTRIBUTIONS FROM THE DYE-HOUSE OF THE YORKSHIRE COLLEGE.

On some New Compounds of Hæmateïn and Brazileïn.

By J. J. HUMMEL and A. G. PERKIN.

WHILE engaged in the preparation of specimens of the colouring principles of logwood, we devised a very simple method for obtaining hæmateïn in the crystalline state in tolerable quantity, which induced us to investigate some of the reactions of this colouring matter.

In order to prepare pure crystalline hæmateïn, commercial logwood extract is dissolved in a small quantity of hot water, and, after cooling, ammonia is added in slight excess to the syrupy solution. The solution of the ammonia-compound of hæmatoxylin thus formed is then exposed to the air for two or three days with occasional stirring, in order to convert it into the corresponding compound of hæmateïn; or this change is effected more rapidly by the aspiration of air through the solution for several hours. A dark purplish precipitate of the ammonia-compound of hæmateïn is gradually deposited. This is collected on a filter and well pressed.

About 40 grams of this precipitate are now dissolved in a litre of hot water, and from 30—160 c.c. of strong acetic acid (sp. gr. 1.04) added. After heating the mixture for some time on the steam-bath (in order to dissolve as much as possible of the amorphous hæmateïn precipitate which has been formed), it is cooled completely and filtered. The amorphous hæmateïn residue on the filter may be treated with hot dilute acetic acid in a similar manner three or four times, and the combined filtrates evaporated over the steam-bath. As the solution becomes concentrated, minute glittering crystals of hæmateïn appear.* In order to separate these from the accompanying impurities, the

* Crystals are also readily obtained when the filtrate from the hæmateïn-ammonia compound is precipitated with excess of acetic acid, the solution filtered and evaporated.

liquid is allowed to cool and mixed with a little acetic acid, which retains these foreign matters in solution, but leaves the hæmatein crystals for the most part undissolved. The latter are collected on a filter, washed three or four times with acetic acid, then with water, and dried.

Thus prepared, hæmatein has the form of exceedingly minute crystals, having a splendid pale yellowish-green metallic lustre.

When viewed under the microscope, they appear by transmitted light as very thin reddish-brown rhombic plates, forming occasionally stellate groups. Rubbed with a glass rod, they yield a reddish-brown powder. Hæmatein is very sparingly soluble in water, alcohol, ether, and acetic acid. Alkalis dissolve it readily; ammonia dissolves it with a rich brown-violet colour; while its strong alkaline soda solution has a rich purplish-blue colour. On exposure to the air, the colour of these alkaline solutions gradually becomes red, and finally brown, the colouring matter being apparently destroyed.

It is worthy of notice that when a very dilute solution of sodium hydrate is added to hæmatein, the latter dissolves with a bright red colour, and only when excess of sodium hydrate is added does the colour become purplish-blue.

Analyses of crystalline hæmatein gave the following numbers:—

0.1270 gram gave 0.3002 gram of CO_2 and 0.0478 gram of OH_2 .

0.1210 " 0.2838 " CO_2 and 0.0466 " OH_2 .

0.1128 " 0.2635 " CO_2 and 0.0419 " OH_2 .

These numbers give percentages agreeing with the formula $\text{C}_{18}\text{H}_{12}\text{O}_6$.

	Theory.	I.	II.	III.
Carbon.....	64.00	64.47	63.94	63.71
Hydrogen ..	4.00	4.18	4.28	4.12

The hæmatein crystals as obtained in the above manner are anhydrous, and evidently identical with those described by Halberstadt and Reis (*Ber.*, 14, 611), who obtained them by extracting aged Campeachy logwood with ether, but were unable to obtain them from commercial logwood extracts.

Action of Sulphuric Acid on Hæmatein.

According to Baeyer (*Ber.*, 4, 457—555), hæmatein is probably a member of the group of bodies termed phthaleins, and possibly stands in a close relationship to gallein.

Since this latter body, when heated for some time with concentrated sulphuric acid to 200° , yields a new green colouring matter termed *coerulein*, it seemed possible that by treating hæmatein in the same

way, a similar product might be formed; but experiment proves that under these conditions the hæmatein is more or less completely destroyed, and yields no new colouring matter. Hæmatein, however, dissolves readily in cold concentrated sulphuric acid, with evolution of heat, producing a dark reddish-brown solution which, when left at rest for some time, becomes filled with lustrous yellow prismatic crystals. When this solution is poured into cold water, it gives a reddish-brown precipitate which resembles ferric oxide, and seems hitherto to have been mistaken for unchanged amorphous hæmatein (see *Gmelin's Org. Chem.*, 10, 293). After washing free from acid, however, it is found to dissolve in sodium hydrate solution with a reddish-purple colour, whereas hæmatein, as already stated, gives a purplish-blue solution. It also dyes mordanted calico in shades quite different from those yielded by hæmatein, viz., with alumina mordants, if weak, it gives a dull red; if strong, red, inclining to chocolate; and with weak iron, a slate. It is evident, therefore, that a new body is produced.

By adding hot glacial acetic acid very gradually, and with constant stirring, to the sulphuric acid solution of hæmatein until it is diluted to the extent of two or three times its bulk, there is gradually thrown down an orange-coloured crystalline precipitate. It is collected on a filter, washed with glacial acetic acid until free from sulphuric acid, and dried. The product thus obtained forms an orange-coloured crystalline powder which, under the microscope, is seen to consist of minute transparent prisms.

On analysis it gave the following numbers:—

0.1120 gram of substance gave 0.2073 gram CO_2 and 0.0331 gram OH_2 .

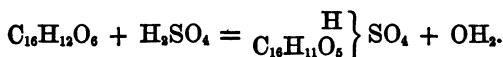
0.1153 gram of substance gave 0.2120 gram CO_2 and 0.0341 gram OH_2 .

0.2325 gram of substance gave 0.1477 gram of BaSO_4 .

These numbers give percentages agreeing with the formula $\text{C}_{16}\text{H}_{11}\text{O}_6 \left\{ \begin{smallmatrix} \text{H} \\ \text{SO}_4 \end{smallmatrix} \right.$.

	Theory.	I.	II.	III.
Carbon.....	50.53	50.47	50.12	—
Hydrogen ..	3.16	3.28	3.29	—
Sulphur	8.42	—	—	8.72

The formation of this body, which we propose to call *acid iso-hæmatein sulphate*, may be represented thus:—



It is insoluble, or nearly so, in alcohol, ether, and benzene, but in strong acetic acid it dissolves to a small extent, forming a yellow solution. It is little soluble in cold ammonia solution, but on heating it dissolves with a dirty claret colour. Its sodium hydrate solution has a reddish-purple colour. Both solutions become brown on exposure to air, very much more rapidly indeed than the corresponding solutions of hæmatein.

When acid isohæmatein sulphate is washed with alcohol, its colour becomes redder, and the filtrate is found to contain a considerable quantity of sulphuric acid. With water it becomes darker than with alcohol, but the same separation of sulphuric acid takes place.

In order to examine this reaction the following preparations were made:—

(1.) A portion of acid isohæmatein sulphate was treated with alcohol, then with water, again with alcohol, and then ether, and dried.

(2.) A second quantity of this substance was treated with water, washed until no more sulphuric acid passed through, and dried.

(3.) A third quantity was placed in contact with ordinary alcohol (about 80 per cent.) and left to stand for some days.

In the course of a few hours the yellow product became covered with dark-coloured patches which were found to consist of crystals, and after two or three days the whole product was found to be converted into these crystals, which, by reflected light, have a beautiful metallic lustre, and, when seen by transmitted light, appear as plates having a dark orange-red colour. This colour is heightened by polarised light. Analyses of these preparations gave the following numbers:—

Preparation I.—0·1109 gram of substance gave 0·2382 gram CO_2 and 0·0339 gram OH_2 .

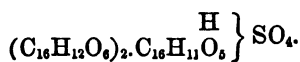
0·1092 gram of substance gave 0·2357 gram CO_2 and 0·0333 gram OH_2 .

Preparation II.—0·1137 gram of substance gave 0·2469 gram of CO_2 and 0·0325 gram of OH_2 .

Preparation III.—0·1059 gram of substance gave 0·2282 gram CO_2 and 0·0358 gram OH_2 .

0·1009 gram of substance gave 0·2167 gram CO_2 and 0·0340 gram OH_2 .

These numbers agree moderately well with the formula—



Theory.	Prep. I.		Prep. II.	Prep. III.	
	I.	II.		I.	II.
Carbon....	58.77	58.55	59.22	58.63	58.57
Hydrogen .	3.67	3.38	3.17	3.75	3.74

From the ready manner in which acid isohæmatein sulphate gives up part of its sulphur as sulphuric acid, it is evident that it is not an ordinary sulphonic acid, but has more the character of an acid sulphuric ether. The remarkable fact, however, is that with water it gives up only two-thirds of its sulphur, yielding the above peculiar body.

On boiling it with magnesium carbonate a large quantity of magnesium sulphate is formed together with a crystalline magnesium derivative, which when freshly prepared is seen to have a metallic lustre. This compound, however, is still found to contain a small quantity of sulphur. After removal of the magnesia by an acid, the product dyes mordants similarly to the original sulphuric product, but the colours are much duller.

It is proposed to examine this product further.

Action of Hydrochloric Acid on Hæmatein.

When hæmatein is heated in sealed tubes with hydrochloric acid (sp. gr. 1.195) for some time to 100°, the rich crimson colour of the solution gradually changes to a dirty yellow, and the mixture is found to contain minute crystals. As soon as the reaction is considered terminated, which is after several hours' heating, the tubes are opened and the contents evaporated to dryness in a dish over the steam-bath.

The product, which consists of a dark, almost black crystalline powder, showing an olive-green metallic lustre when viewed under the microscope, may be purified by heating it with water, slightly acidulated with hydrochloric acid, in which it easily dissolves, and filtering. On adding hydrochloric acid to the rich orange-coloured filtrate, an orange precipitate is obtained, and if the whole be now boiled so as to redissolve the product, there is deposited on cooling a red powder, which appears under the microscope to consist of minute transparent orange-red needles.

This substance was found to contain chlorine.

On analysis the following numbers were obtained :—

0.1239 gram of substance gave 0.2729 gram of CO₂, and 0.0402 gram OH₂.

0.1277 gram of substance gave 0.2808 gram of CO₂, and 0.0411 gram OH₂.

0.2169 gram of substance gave 0.0878 gram of AgCl.

0.2053 gram of substance gave 0.0856 gram of AgCl.

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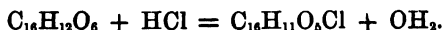
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These numbers give percentages agreeing with the formula



	Theory.	I.	II.	III.	IV.
Carbon	60.28	60.07	59.96	—	—
Hydrogen ..	3.45	3.60	3.57	—	—
Chlorine	11.15	—	—	10.59	10.82

The formation of this body may be expressed thus :—



This was found to take place almost quantitatively, as will be seen from the following experiment :—

0.2904 gram of hæmatein, heated with concentrated hydrochloric acid, increased in weight 5.74 per cent. Theory requires 6.13.

We propose to call this substance *Isohæmatein Chlorhydrin*. It dissolves easily in water, forming an orange-coloured solution, which is rather strongly acid, owing to the separation of hydrochloric acid, and if repeatedly evaporated and redissolved, loses most of its chlorine. It is less soluble in alcohol than in water. With alcoholic potash it gives a reddish-violet solution, which soon changes and becomes slaty, and afterwards of a blackish-brown colour, the intensity quickly diminishing.

With concentrated sulphuric acid it evolves hydrochloric acid gas, and is converted into acid isohæmatein sulphate. It dyes mordants in a similar manner to the sulphuric compound, but much more freely, and the shades are rather brighter in tone.

Action of Hydrobromic Acid on Hæmatein.

When hæmatein is heated in sealed tubes with strong hydrobromic acid, the *corresponding isohæmatein monobromhydrin* is produced.

The product consists of a dark mass of microscopic needles.

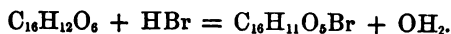
On analysis it gave the following result :—

0.2572 gram of substance gave 0.1274 gram of AgBr.

The percentage from this agrees closely with that required by the formula $\text{C}_{16}\text{H}_{11}\text{O}_5\text{Br}$.

	Theory.	I.
Bromine	22.03	21.60

The reaction may be expressed thus :—



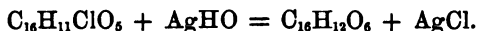
Isohæmatein bromhydrin dissolves in alkalis, with a violet colour,

and altogether in its general properties resembles the chlorine compound.

Isohæmatein.

If to an aqueous solution of *isohæmatein chlorhydrin* or *bromhydrin* enough argentic hydrate be added to remove the chlorine, the dark orange solution becomes somewhat less bright, and darker in colour. This solution when concentrated on the water-bath and then evaporated to dryness over sulphuric acid, leaves *isohæmatein* as an amorphous mass with a green metallic lustre.

This product has not yet been obtained perfectly pure and quite free from chlorine, but on analysis it gives numbers indicating that it has the same composition as hæmatein. The formation of this body may be expressed thus:—



It is, however, an isomeride of that body, and differs from it considerably in its properties, as the following comparison will show:—

	Hæmatein.	Isohæmatein.
Solution of caustic alkali	Blue-violet colour.	Red-violet colour.
„ sodium carbonate ..	Reddish-purple colour.	Purple.
Ammonia	Bright red-purple.	Dull red-purple.
Ammonium sulphide	Nearly decolorised, but quickly becoming purple when placed on bibulous paper, and exposed to the air.	A red-purple precipitate.
Solution of lead acetate	Blue violet precipitate.	Red-purple precipitate.

Isohæmatein dyes mordants much in the same way though not so freely as *isohæmatein chlorhydrin*, and not at all like hæmatein. It is also more soluble in water than that colouring matter.

Brazilein.

Crystalline *brazilein* is obtained from commercial Brazilwood extracts by a method exactly similar to that employed for the production of crystalline hæmatein, only that it is necessary, after treating the extract with ammonia, to expose the solution to the air for a greater length of time, the oxidation in this case taking place more slowly. Obtained in this manner *brazilein* has the form of very minute dark crystals, having a grey metallic lustre, and forming when rubbed a brown-red powder. Under the microscope they appear as thin reddish-brown rhombic plates, sometimes grouped together in the

form of rosettes, but for the most part they are detached and lens-shaped, with the points of the lens cut off obliquely.

It is very slightly soluble in cold water, but more so in hot, the solution having a pale yellowish-pink colour, with a distinct greenish-orange fluorescence; alkalis dissolve it, forming rich carmine-red solutions, which, although much more stable than the corresponding compounds of hæmatein, gradually become brown when exposed to the air. There is but little difference in the colour of the ammonia and sodium hydrate solutions of brazilein.

Dried at 130° it gave on analysis the following numbers:—

0.1071 gram of substance gave 0.2644 gram CO₂, and 0.0408 gram OH₂.

0.1024 gram of substance gave 0.2531 gram CO₂, and 0.0390 gram OH₂.

These numbers give percentages agreeing with the formula



	Theory.	I.	II.
Carbon	67.60	67.30	67.46
Hydrogen	4.22	4.22	4.23

But dried at 100° these crystals were found to contain one molecule of water, which is given off at from 130° to 140°.

0.1137 gram at 100° became 0.1071 gram at 130°.

0.1090 „ 100° „ 0.1054 at 130°.

	Theory.	I.	II.
	5.96	5.97	6.05

Analysis of samples dried at 100° gave the following numbers:—

0.1193 gram of substance gave 0.2790 gram CO₂, and 0.0485 gram OH₂.

0.1386 gram of substance gave 0.3231 gram CO₂.

These numbers give percentages agreeing with the formula



	Theory.	I.	II.
Carbon	63.57	63.78	63.57
Hydrogen	4.63	4.51	—

Action of Sulphuric Acid on Brazilein.

Brazilein gradually dissolves in cold concentrated sulphuric acid, forming a dark orange-coloured solution, which when dilute has a

very marked olive-green fluorescence. On long standing the solution becomes filled with lustrous yellow rhombic needles.

If the solution be poured into water, a bright orange-coloured amorphous precipitate is thrown down, which represents a new body. By adding to the sulphuric acid solution hot glacial acetic acid in small quantities at a time, and with constant stirring, the new product is gradually thrown down in the form of minute crystals. These are thrown on a filter, thoroughly washed with glacial acetic acid, and dried.

Thus obtained it consists of an orange-coloured crystalline mass, seen under the microscope to consist of transparent flat needles.

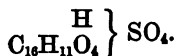
On analysis the following numbers were obtained:—

0.1191 gram of substance gave 0.2297 gram CO_2 , and 0.0364 gram OH_2 .

0.1055 gram of substance gave 0.2037 gram CO_2 , and 0.0325 gram OH_2 .

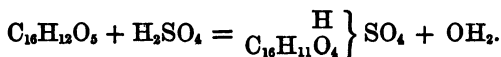
0.1102 gram of substance gave 0.2111 gram CO_2 , and 0.0334 gram OH_2 .

These numbers give percentages agreeing with the formula



	Theory.	I.	II.	III.
Carbon	52.74	52.59	52.68	52.24
Hydrogen	3.29	3.39	3.42	3.36

The formation of this body may be expressed thus:—



This *acid isobrazilein sulphate* as we propose to name it, is only slightly soluble in boiling glacial acetic acid, but very soluble in alkalis. Its ammonia solution has a rich carmine colour, almost identical with that of the corresponding solution of brazilein. Its soda solution is somewhat bluer in tint. Both solutions rapidly become brown when exposed to the air very much more rapidly than the alkaline solutions of brazilein.

On treatment with alcohol, these crystals become bright scarlet in colour, and on filtering, the filtrate is found to contain sulphuric acid in considerable quantity.

Under the microscope the product now appears as brilliant red needles. It is slightly soluble in water, alcohol, and acetic acid.

On analysis this body gave the following numbers:—

0.1158 gram of substance gave 0.2426 gram of CO_2 , and 0.0400 gram of OH_2 .

0.0712 gram of substance gave 0.1478 gram of CO_2 , and 0.0239 gram of OH_2 .

0.1433 gram of substance gave 0.2970 gram of CO_2 and 0.0452 gram of OH_2 .

These results give numbers corresponding with the formula



	Theory.	I.	II.	III.
Carbon	56.90	57.13	56.61	56.50
Hydrogen	3.55	3.83	3.73	3.50

The sulphuric derivatives of brazileïn dye mordants differently from brazileïn itself, and yield colours somewhat like those of garancin.

Action of Hydrochloric Acid on Brazileïn.

Brazileïn digested in sealed tubes with concentrated hydrochloric acid at 100° behaves in a very similar manner to hæmateïn. The reaction, however, takes place much more slowly. The solution, which at first has a bright scarlet colour, gradually changes to a dirty yellow, and crystals separate out.

As soon as the reaction has terminated, which is generally after eight or ten hours' heating, the whole is evaporated to dryness over the steam-bath. The product consists of a very dark brown crystalline mass, having a violet lustre. Under the microscope it exhibits the form of small prisms having the colour of potassium bichromate by transmitted light.

On analysis it gave the following numbers:—

0.1436 gram of substance gave 0.3335 gram of CO_2 , and 0.0473 gram of OH_2 .

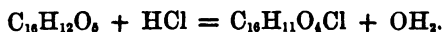
0.1179 gram of substance gave 0.2725 gram of CO_2 , and 0.0387 gram of OH_2 .

These numbers give percentages agreeing with the formula



	Theory.	I.	II.
Carbon	63.13	63.28	63.03
Hydrogen	3.66	3.65	3.64

The formation of this substance may be expressed thus:—



Isobrazileïn chlorhydrin, as we have named this body, dissolves readily in water, forming an orange-coloured solution, which is acid to litmus-paper and contains free hydrochloric acid. Its alkaline solutions have a slight greenish fluorescence.

Action of Hydrobromic Acid on Brazileïn.

On adding fuming hydrobromic acid in excess to brazileïn, it dissolves to a small extent, and at the same time changes the undissolved portion to a beautiful carmine. On heating the mixture in a sealed tube to 100° this substance mostly dissolves, forming a red solution, which gradually changes into an orange-yellow coloured liquid. After heating for five or six hours, the undissolved portions of the product are seen to consist of crystals. On cooling, most of the product separates out as crystals, which, when seen under the microscope, appear as flat oblique prisms, their colour by transmitted light being like that of potassium bichromate, but darker.

On analysis, the following numbers were obtained:—

0.1576 gram of substance gave 0.3190 gram of CO_2 and 0.0460 gram of OH_2 .

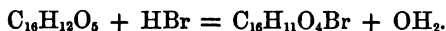
0.1613 gram of substance gave 0.3260 gram of CO_2 and 0.0498 gram of OH_2 .

These numbers give percentages agreeing with the formula



	Theory.	I.	II.
Carbon	55.33	55.2	54.9
Hydrogen	3.17	3.23	3.40

The formation of this body, which we have named *Isobrazileïn bromhydrin*, may be expressed thus:—



When ground logwood is boiled for some time with dilute sulphuric or hydrochloric acid and then well washed, it dyes mordants in a similar manner to the hæmatein derivatives. This is probably owing to the formation of an analogous hæmatoxylin derivative which oxidises during the process of dyeing. Brazilwood also behaves in a similar matter when treated with acids.

Other acids besides those mentioned, namely, oxalic, tartaric, &c., yield evidently analogous compounds. Nitric acid, too, appears to give a similar compound, but it is difficult to control the reaction.

Heated to 120° with phthalic anhydride for some time, hæmatein yields also a new colouring matter.

Further experiments on the action of these various substances on hæmatein are in progress.

The tinctorial power of the new compounds is much greater than that of the original hæmatein and brazilein, and a very noteworthy point is that the colours are much faster, withstanding the action of a boiling soap-solution, and a weak solution of bleaching powder tolerably well, especially those derived from the brazilein.

During the dyeing process, the whites are considerably soiled, and this, in most cases, is probably due to the liberation of the acids from the compounds when in contact with water, the liberated acid causing the mordant to dissolve and then attach itself to the unmordanted portions of the cloth.

The new hæmatein compounds give on cotton mordanted with alumina a dull red inclining to chocolate, with strong iron a black, with weak iron a slate, and with mixed alumina and iron mordant a full chocolate.

The sulphuric derivatives of hæmatein, however, produce shades with alumina mordants somewhat redder than the other products. Soaping renders all the colours produced by these compounds rather bluer in tone.

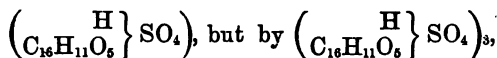
The brazilein derivatives with the same mordants give shades resembling those of the hæmatein compounds. They possess, however, a much more lively red tint, and in fact remind one of the corresponding garancine shades.

The foregoing results show how very similarly hæmatein and brazilein behave towards reagents, and confirm the views of Liebermann respecting their relationship (*Ber.*, 9, 1883). The ease with which they exchange one, and only one, hydroxyl for chlorine or bromine when treated with the corresponding haloïd acids, and the readiness with which the resulting products give up these elements again when treated with water or bases, is remarkable, and points out that this hydroxyl is not phenolic but most probably alcoholic.

The fact that these bodies, when giving up their chlorine or bromine on treatment with silver oxide or other bases, do not regenerate hæmatein or brazilein, but yield substances isomeric with them, shows either that some change takes place in the molecule itself, or else that it becomes polymerised. The fact that the products are more soluble in water than either hæmatein or brazilein is, perhaps, rather against this latter view, but in the case of the sulphuric derivatives polymerisation is believed to take place. As already stated, these substances appear to be somewhat analogous to the acid sulphuric ethers, and in fact they are decomposed by water, with separation of sulphuric acid, even more readily than these bodies; but this decomposition is only

partial, and results in the formation of products which cannot be represented as derived from less than 3 mols. of the original colouring matter.

It is therefore inferred that acid isohæmateïn sulphate should be represented, not by the formula



and the analogous brazileïn compound as $\left(\text{C}_{16}\text{H}_{11}\text{O}_4 \right\} \text{SO}_4)_3$. These products are moreover difficultly soluble in most fluids, which also points to the same fact.

Although it has been up to the present found impossible to produce from hæmateïn a body similar to the coeruleïn obtained from galleïn, it does not prove that hæmateïn does not belong to the class of phthaleïns. On the contrary, our experiments appear rather to confirm this view of Baeyer, as among the phthaleïns there are several which are already known to form somewhat peculiar compounds with sulphuric and hydrochloric acids, *e.g.*, fluoresceïn and phthaleïn-orcin (*Ber.*, 7, 1213—1214), quinol-phthaleïn (*Ber.*, 11, 715), and homofluoresceïn (*Ber.*, 13, 547).

The formation, instability, and composition of these compounds apparently show that they are analogous to the acid-compounds of hæmateïn and brazileïn described in this paper.

LIX.—*On the Crystallisation from Supersaturated Solutions of certain Compound Salts.*

By JOHN M. THOMSON, and W. POPPLEWELL BLOXAM; King's College, London.

In a paper published in the Chemical Society's Journal, May, 1879, on "The Action of Isomorphous Salts in producing the Crystallisation of Supersaturated Saline Solutions," I pointed out that if a mixture of dimorphous salts be taken, a separation of the salts may be effected within certain limits by touching the solution with a crystal of one or other of the salts, this separation being limited by and depending on the relative solubilities of the different salts contained in the solution.

The subject of the present paper is a continuation of these observations, employing in this case supersaturated solutions of double salts,

where it was possible to obtain such, and acting on them with nuclei consisting of one or other of the component salts, in order to find whether any disruption of the compound has taken place by the action of the nucleus. The method of carrying out the experiments was exactly the same as that employed before, and fully described in my first paper, the nucleus being added to the solution to be experimented on by one of two methods: (1) the nucleus being obtained by crystallisation from a supersaturated solution, and in this condition retained in the syphon-tube in the neck of the flask till required for use: or (2) the nucleus being added directly from its mother-liquor in a bulb-tube suspended in a similar manner in the neck of the flask.

In all these experiments, as before, the substances were purified with the greatest care, and the admission of particles from the external air most carefully guarded against.

The first group of salts experimented with consisted of certain of the double chlorides, bromides, and iodides of mercury with the corresponding salts of the alkali-metals. The results obtained with these bodies are detailed in the following table:—

Substance in solution.	Nucleus added.	Result.
HgCl ₂ (NH ₄ Cl) ₂ ,3H ₂ O ..	HgCl ₂ (prismatic)	Active.
„ ..	HgCl ₂ (deposited from hot solution)	Both active and inactive.
„ ..	NH ₄ Cl.....	Inactive.
HgBr ₂ (NH ₄ Cl) ₂ ,3H ₂ O ..	HgBr ₂ (deposited in the cold)	Active.
„ ..	HgBr ₂ (deposited from hot solution)	Both active and inactive.
„ ..	(NH ₄)Br.....	Inactive.
HgI ₂ (KI) ₂	HgI ₂ (needle-shaped crystals)	Active.
„	KI	Inactive.
HgCl ₂ (NH ₄ Cl) ₂ ,3H ₂ O ..	HgBr ₂ (NH ₄ Br) ₂ ,3H ₂ O	Active.
HgBr ₂ (NH ₄ Br) ₂ ,3H ₂ O .	HgCl ₂ (prismatic).....	Active.
„ ..	NH ₄ Cl.....	Inactive.

It is very difficult to obtain many double salts of the halogen acids in a state of supersaturation, and the field for experiment with them is therefore limited. In the cases described above, however, there are several points to be noticed. With these double salts the salt of the heavy metal invariably caused the crystallisation of the double salt,

whereas the constituent containing the alkali-metal had no action. It was, however, impossible to determine whether the salt causing crystallisation did so by first inducing the deposition of the salt analogous to itself in the solution. Experiments are being carried out to endeavour if possible to determine the primary action which takes place; it is, however, a somewhat difficult one to examine.

It may also be observed that when the mercuric chloride or bromide existed in the nucleus in its true prismatic form, crystallisation at once took place, but that when its deposition from its solution took place at a higher temperature the results were various. On examining this point, I find that the crystalline forms of the mercuric chloride and bromide change when so deposited, which may readily account for the alternation in those cases. The crystalline form also of the double salt is more nearly allied to the form of the heavy metallic salt, than to the constituent containing the alkali-metal.

Finding that a double salt consisting of mercuric cyanide with ammonium chloride ($\text{HgCy}_2, \text{NH}_4\text{Cl}$) existed, forming a good supersaturated solution, I made experiments in order to compare it with the double salts before mentioned; when the following results were obtained:—

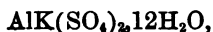
Substance in solution.	Nucleus added.	Result.
$\text{HgCy}_2, \text{NH}_4\text{Cl}$	HgCy_2	Active.
„	NH_4Cl	Active.

In this case there is a distinct difference from the halogen salts employed in the first-mentioned experiments, both components producing the crystallisation of the double salt.

It seems probable, therefore, that the double salts formed from these monobasic acids, although they form good supersaturated solutions, are not so firmly united together as to withstand the disturbing influence of certain of their constituents; but that the disruption produced by them is not sufficient to cause the decomposition of the body, and consequently the double salt is deposited. In the case last mentioned also, of the double cyanide and chloride, both salts are deposited as the final result of the crystallisation.

In experimenting with mercuric iodide, this substance was introduced by means of a pipette-shaped tube, and the iodide strongly steamed by boiling the flask before it was allowed to cool.

The next double salt examined was ordinary potash-alum



as this salt undergoes supersaturation with very great ease, and may be taken as a good instance of a thoroughly well defined double salt from a bibasic acid. The following results were obtained:—

Substance in solution.	Substance added.	Result.
$\text{AlK}(\text{SO}_4)_2, 12\text{H}_2\text{O} \dots$	$\text{Al}_2\text{S}(\text{SO}_4), 18\text{H}_2\text{O} \dots$	Inactive.
„	$\text{K}_2\text{SO}_4 \dots \dots \dots$	Inactive.

showing that neither of the constituents from which the double alum is originally derived, has any action upon its supersaturated solution. This is the more interesting, when it may be remembered that the late Dr. Graham held the view that potash-alum might be split up into its constituents by the process of dialysis. The alum solution used in my experiments was saturated at 90°C .

Other Observations on Supersaturated Alum Solutions.—In connection with the main object of the examination of these solutions, certain other experiments were made which yielded results of sufficient interest to warrant their being mentioned. Cold saturated solutions of potassium and aluminium sulphates at a temperature of 15°C . were mixed together, when it was observed that considerable rise in temperature took place, amounting generally with the mass of substance used to about 15° . At the same time a deposition of crystals took place which on examination were found to be alum, corresponding to the composition $\text{AlK}(\text{SO}_4)_2, 12\text{H}_2\text{O}$. These experiments were repeated many times, the result always being the same.

Some very curious peculiarities were observed with an alum solution saturated at 95° , a temperature slightly higher than that at which the ordinary solutions were prepared. This solution was stoppered with cotton-wool in the ordinary way, and set aside to cool. When it had attained a temperature nearly that of the surrounding air, small opaque crystals began to form in the liquid, and crystallisation gradually proceeded, without, however, the production of heat-currents in the liquid, which is so marked an accompaniment of the more rapid crystallisation from a supersaturated solution. In about four hours the whole contents of the flask, except a thin layer at the bottom, were apparently perfectly solid and the flask quite cold. On touching the solid, however, with a glass rod, and finally stirring the pasty contents of the flask, a great evolution of heat took place, equal to that observed in the ordinary crystallisation of a supersaturated solution of alum. The formation of the crystals in this case was extremely peculiar, and appeared to be accompanied by some contraction causing the mass to creep away from the sides of the flask, which contraction might possibly account for the non-evolution of any large quantity of heat during solidification.

As the same phenomenon was observed with this solution over and over again on its cooling, I determined to examine the crystals deposited by suddenly breaking the flask, and washing its solid contents with ice-cold water. This was accordingly done, and the crystalline

mass, after air-drying, yielded on analysis numbers very closely corresponding with ordinary alum. An examination of the crystalline form of the body deposited showed, however, that the aggregation of the crystals was quite different from the formation deposited from a proper supersaturated solution, the crystals being small, and arranged in tree-like forms like ammonium chloride. It is difficult, however, to examine them accurately, as on touching or moving they are converted into the usual octohedra of alum. From these last-mentioned experiments it would appear that above, say 90° , the limit of supersaturation for alum is passed. There is also some indication of a dimorphous form of alum existing. Another fact with regard to this alum-solution may be mentioned, viz., that after it had solidified, on immersing the *cold* flask in boiling water to remelt the salt, it was observed; first, that the water continued to boil, and, secondly, that the contents of the flask underwent reliquefaction after about ten minutes' immersion; whereas, in ordinary cases, the solution of the same quantity of deposited alum is very gradual, and would take about sixty minutes.

I was anxious to compare the alum experiments with the double sulphates formed from protoxides of the same group, such as the double sulphates of iron and zinc with potassium sulphate, of the general formula $M''K_2(SO_4)_6 \cdot 6H_2O$, but it was found that these sulphates have no tendency to undergo supersaturation—at least to an extent sufficient for our experiments.

I next prepared a supersaturated alum solution by dissolving equivalent quantities of $Al_2(SO_4)_3 \cdot 18Aq$ and K_2SO_4 in a quantity of water exactly corresponding with that which would have been necessary for the solution, had crystallised alum been used instead of the constituents separately. It was found, however, that with the two salts taken separately in the manner described, the quantity of water was not sufficient for their entire solution, and had to be increased by an amount corresponding with nearly one-half of the original quantity taken, before perfect solubility could be obtained. With this solution, however, it was found that neither crystals of $Al_2(SO_4)_3 \cdot 18H_2O$ nor K_2SO_4 were at all active; but the moment it was touched with $AlK(SO_4)_2 \cdot 12H_2O$, the liquid became filled with crystals of alum.

Being unable to obtain good supersaturated solutions of the double sulphates represented by the general formulæ $M''K_2(SO_4)_6 \cdot 6H_2O$ and $M''M''K_4(SO_4)_4 \cdot 12H_2O$, which have been described by Vohl (*Annalen*, 95), I determined to try some experiments with a double sulphate of zinc and copper, known as Lefort's salt, the composition of which, according to that author, is $Zn_3Cu(SO_4)_4 \cdot H_2O$, and which will undergo recrystallisation without decomposition.

Quantities of this salt were dissolved in rather less than half their

weight of water, zinc sulphate ($\text{ZnSO}_4, 7\text{H}_2\text{O}$) and copper sulphate ($\text{CuSO}_4, 5\text{H}_2\text{O}$) being employed as the nuclei.

In these cases both the constituents were active in causing crystallisation, that from the zinc sulphate nucleus being more rapid than that from the copper sulphate nucleus. An examination of the crystals deposited showed that they were crystals of the double salt, and their deposition presented some very peculiar phenomena. When the zinc sulphate was employed, the crystals of the double salt are formed first in long shaped needles, closely resembling those of $\text{ZnSO}_4, 7\text{H}_2\text{O}$; this form is retained till the crystallisation is very nearly at an end, but shortly afterwards the crystals gradually begin to change, and break up into truncated needles exactly similar to Lefort's salt.

In the case of the copper sulphate nucleus, the deposition of the salt was slower, and the crystals, though not doubly oblique like $\text{CuSO}_4, 5\text{H}_2\text{O}$, were truncated needles, and never came down in long needles as in the first mentioned case. The deposit here was also found to be the double salt.

From these experiments it will be seen that the nucleus in certain cases exercises a determining influence on the crystals of the body deposited, in a manner similar to some other cases mentioned in my first paper.

This I think may be due, at least in the case of the zinc sulphate, to the nucleus of that salt beginning the action by separating first $\text{ZnSO}_4, 7\text{H}_2\text{O}$ crystals; but the forms of both the constituents being to a certain extent similar, it gradually induces the crystallisation of the copper salt as well, and the double salt is deposited.

Some curious phenomena were to be observed in the deposition of the crystals from these solutions, when the nucleus became detached from the introducing tube and fell to the bottom of the flask. In such cases when the nucleus was moved along the bottom of the flask by slightly inclining it, crystallisation was observed to take place, first along the line upon which the nucleus had travelled, and it was some little time before crystallisation extended in other directions throughout, showing that crystalline activity had been induced directly by the nucleus.

Experiments with Microcosmic Salt, $\text{Na}(\text{NH}_4)\text{HPO}_4, 4\text{Aq}$.

The experiments on solutions of this body were made in the same way as on the other substances, the nuclei being added both with the syphon-tube and with the bulb-tube.

Substance in solution.	Nucleus added.	Result.
$\text{NaNH}_4\text{HPO}_4, 4\text{H}_2\text{O}$..	$\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$..	Inactive.
" ..	$(\text{NH}_4)_2\text{HPO}_4$	"
" ..	$(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$	"
" ..	$\text{Na}_4\text{P}_2\text{O}_7$	"

It was found extremely difficult to obtain the ammonium phosphates free from sodium, many weeks being taken up in preparing good samples. They were finally obtained by neutralising perfectly pure phosphoric acid by ammonium carbonate. There are also several points with regard to the composition of the ammonium phosphates, which require further investigation.

In the case of microcosmic salt, on attempting to form it from cold saturated solutions of the disodic and diammonic phosphates, the same result was observed as in the case of alum, the solution when brought in contact undergoing a considerable rise in temperature, and crystals of microcosmic salt being deposited. The rise in temperature in these cases was less than in the alum experiments, being generally an increase of from 10° to 12° .

In connection with these double phosphate experiments, others were made with the double arsenate of sodium and ammonium, with the following results:—

Substance in solution.	Nucleus added.	Result.
$\text{NaNH}_4\text{HAsO}_4 \cdot 4\text{H}_2\text{O} \dots$	$\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O} \dots$	Inactive.
„ „	$(\text{NH}_4)_2\text{HAsO}_4 \cdot 4\text{Aq} \dots$	„

In these cases both constituents were inactive to the double salt, as in the case of the alum and the phosphates.

Action of the Constituents on Supersaturated Solutions of Double Tartrates and Citrates.

It is not easy to find double salts of organic acids which will undergo supersaturation without passing into a gummy consistency which precludes experiment. The substances, however, which we have been able to employ are the double tartrate of sodium and potassium or Rochelle salt ($\text{KNaH}_4\text{C}_4\text{O}_6 \cdot 4\text{Aq}$); the double potassium and sodium citrate, $\text{K}_3\text{Na}_3(\text{H}_3\text{C}_6\text{O}_7)_2$; and the double magnesium and sodium citrate, $\text{MgNaH}_5\text{C}_6\text{O}_7$. The methods of adding the nuclei were similar to those employed in the other cases, as the constituents undergo supersaturation with great readiness.

With Rochelle salt the following results were obtained:—

$\text{KNaH}_4\text{C}_4\text{O}_6 \cdot 4\text{Aq} \dots$	$\text{K}_2\text{H}_4\text{C}_4\text{O}_6 \dots$	Inactive.
„ „	$\text{Na}_2\text{H}_4\text{C}_4\text{O}_6 \dots$	Active.

The sodium tartrate was specially made and perfectly purified. In all these cases crystallisation from the sodium tartrate took place, but never from the potassium tartrate. It now became important to examine if possible the composition of the crystals which were gradually deposited from the nucleus. For this purpose experiments

were carefully performed in flasks containing the Rochelle salt, to which the nuclei of neutral sodium tartrate were added by means of the syphon-tubes. The crystals gradually and slowly formed from the point of the syphon-tube, and were allowed to grow till a considerable cluster had formed, and a great part of the salt had been thus removed from the solution in the flask. The deposit adhering to the syphon-tube was withdrawn from the mother-liquor removed from the flask, washed with ice-cold water, pressed between blotting-paper, air-dried, and analysed. On analysis the deposit gave numbers closely agreeing with the composition of Rochelle salt.

Now it is to be observed that the crystals forming the deposit here in no wise resemble those of Rochelle salt, but closely resemble those of sodium tartrate, giving us evidence of the probable dimorphism of Rochelle salt. We have also to note that if the crystals formed by the nucleus of sodium tartrate are allowed to grow till the contents of flask are nearly solid, and then rinsed from the mother-liquor, this mass being then stirred, a sudden and considerable amount of heat is evolved, as in the case of the alum solution before mentioned. After stirring the mass and examining the crystals by the microscope, they present the appearance of ordinary Rochelle salt.

At present it is difficult to see why the sodium tartrate should be active and the potassium salt inactive, but it may be remarked that the solubility of the sodium salt is less than that of the potassium salt, which may perhaps account for its activity. A corresponding result has been observed with the citrate of potassium and sodium, in which the sodium citrate has always proved active, whilst the potassium salt is inactive. Here also the solubility of the potassium salt is greater than that of the corresponding sodium salt.

In the case, however, of the double magnesium and sodium citrates, the results were different, both of the constituent salts proving inactive to the double salt.

From these experiments it will be seen that the double salts of monobasic acids apparently suffer disruption more easily than the salts from acids of higher basicity like sulphuric and phosphoric acids; but that in the case of the first of these two latter acids, salts may exist, like Lefort's salt, which is acted upon by the constituents.

It will be observed, however, that such salts indicate more of molecular than of atomic grouping in their constitution, whereas in the true alum and double phosphate we have a firmer union of the salts. This is also, I think, to be observed in the salts from the organic acids. By its mode of formation and its composition, the double sodium and potassium citrate appears more like a molecular grouping of the constituent salts, and both constituents are capable of causing disruption, whereas in Rochelle salt and the magnesio-sodic

citrate, there is evidence of a closer binding of the component salts. In the case of Rochelle salt, only one constituent produces disruption, and in the case of the magnesio-sodic citrate, neither constituent has any action. It is to be hoped that further experiments carried out on these solutions may assist in the examination of the condition of such salts when in a state of solution.

I am at present engaged on certain experiments with regard to the amount of heat evolved in the crystallisation of these compound salts, and comparing the numbers obtained in the different groups of salts. These experiments take much time to carry out, but I hope soon to be in a position to lay the results before the Society.

LX.—On *Oxypropyltoluidine*.

By H. FORSTER MORLEY, M.A., Fellow of University College.

PROPYLENE oxide dissolves an equivalent quantity of paratoluidine, producing a fall of some 15° in temperature. The solution was heated in a water-bath for four hours, and the viscid liquid thus formed was submitted to distillation; it contained no propylene oxide, and only a drop or two of toluidine, but the thermometer rose rapidly to 280° , remained constant for some time at 285° — 288° , and finally reached the boiling point of mercury before the liquid had all passed over.

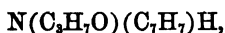
The portion boiling above 360° contains, no doubt, dioxypropylene-toluidine.

The chief portion (285° — 296°) solidified after some time, and was analysed after recrystallisation from a small quantity of benzene.

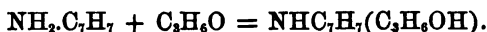
- I. 268 gram substance gave 0.7166 gram CO_2 and 2.243 gram H_2O .
 II. 256 gram gave 17.7 c.c. N at 11°C , bar. press. 782 at 13° .

Whence	Calculated for oxypropyltoluidine.	Found.
C	72.73	72.92
H	9.09	9.30
N	8.48	8.39

The numbers agree therefore with the formula—



and the reaction may be represented by the equation—



A better yield is obtained by avoiding the use of heat, and simply allowing the solution of toluidine in propylene oxide to stand for some days at the ordinary temperature. The limpid liquid then becomes gradually viscid, and at length the new base crystallises out. It may be separated from the mother-liquor by filtration and pressure, and recrystallised from light petroleum oil, when it is obtained in the form of slender needles.

In this way 20 grams of the base were obtained from 46 grams of toluidine.

A third method consists in converting the bases into oxalates and separating them by crystallisation from water.

The oxalate of the new base is very soluble; that of toluidine is, as is well known, nearly insoluble, while other oxalates present have intermediate solubility.

Oxypropyltoluidine melts at 74° and boils with slight decomposition at 293° (corr.); it has not much tendency to become coloured when exposed to air; it is insoluble in water, but soluble in benzene, ether, alcohol, and petroleum.

I have not been able to obtain its chloride, sulphate, chloroplatinate, or chloroaurate in crystalline form.

If the base be dissolved in aqueous oxalic acid and the solution concentrated by evaporation, crystals of the oxalate are formed; these may be recrystallised from water or spirit, when they form pearly plates melting at 151° .

The analysis of these crystals gave the following result:—

- I. 2686 gram was decomposed by CaCl_2 and the calcic oxalate converted into lime by ignition, 059 gram CaO .
- II. 2495 gram gave as combustion 5176 CO_2 and 1558 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_{15}\text{NO}, \text{H}_2\text{C}_2\text{O}_4.$	Found.
C	56.47	56.58
H	6.67	6.94
$\text{H}_2\text{C}_2\text{O}_4$	35.29	35.29

The compound is therefore the acid oxalate of oxypropyltoluidine, and it appears to be the only one capable of existing, for if excess of base (2 mols.) be dissolved in spirit and mixed with an alcoholic solution of oxalic acid (1 mol.), the acid oxalate crystallises out first, and afterwards the free base separates in needles.

It is to be observed that the neutral oxalate of *p*-toluidine is not known.

When the oxalate is heated to 150° it melts, and then gives off water, carbonic oxide, and carbonic acid, and leaves a non-crystallisable syrup, which is only partly basic (soluble in aqueous oxalic acid); the insoluble part begins to boil at about 270°.

I had hoped to find among the products of this reaction a base of the formula $C_{10}H_{13}N$, formed from oxypropyltoluidine by dehydration, and possibly belonging to the quinoline series, but I have not succeeded in isolating such a base.

I will take this opportunity of describing the—

Distillation of Oxypropyltrimethylammonium Hydrate.

This base, which I have described elsewhere (this Journal, 38, 877) resembles ordinary neurine in its behaviour when heated; it first froths up, giving off trimethylamine, then propylene-glycol and other liquids come over, and finally carbonic acid is evolved.

The products were passed, first into a cold tube, then through dilute hydric chloride, next through lime-water, and finally into bromine (which did not, however, absorb any olefine).

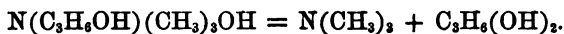
The platinum salt of trimethylamine obtained from the hydric chloride solution was ignited.

·3544 gram contained ·1314 gram platinum.

	Theory.	Found.
Pt	37·38	37·08

The chief portion of the liquid distillate is propylene-glycol, recognised by its boiling point, sweet taste, and miscibility with water, alcohol, and ether.

It is formed by the equation—



The propylene-glycol is, however, mixed with small quantities of volatile bases produced by secondary reactions, but of which I have not obtained sufficient for identification.

LXI.—On some Halogen Compounds of Acetylene.

By R. T. PLIMPTON, Ph.D.

BERTHELOT has shown that acetylene unites with the halogen elements, forming compounds of the formulæ $C_2H_2X_2$ and $C_2H_2X_4$. Of such derivatives, the di- and tetra-chlorides and bromides, and a di-iodide are known; also an iodide, $C_2H_2I_4$, obtained by the action of iodine upon silver acetylide.

The present paper contains a few additional observations upon some of the above, and on the preparation and properties of the remaining di-derivatives, *i.e.*, the chlorobromide, chloriodide, and bromiodide.

The acetylene needed for the following experiments was obtained by burning coal-gas in the apparatus described by Jungfleisch (*Bull. Soc. Chim.*, 31, 482), passing the products through ammoniacal cuprous chloride solution, and decomposing the precipitate with hydrochloric acid in the usual way.

Acetylene Bromides.

By the action of bromine on acetylene, Berthelot obtained a dibromide boiling at 130° , and a tetrabromide. Under ordinary conditions, however, when the gas is passed through bromine, the products are, as shown by Reboul (*Compt. rend.*, 54, 1229) and Sabanejeff (*Annalen*, 178, 112), the tetrabromide and a small quantity of a solid body, C_2HBr_3 , crystallising in laminæ and melting at 174° . I obtained the same results.

By treating the tetrabromide mixed with its own volume of alcohol, with zinc powder, as recommended by Sabanejeff (*Ber.*, 9, 1441), a considerable quantity of dibromide was prepared. It boiled at 110 — 111° , and did not solidify at -17° . Its specific gravity at 0° was 2.268.

The results of some experiments upon the action of tertiary amines on this bromide have already been communicated (*Trans.*, 1881, 536).

Acetylene Iodides.

The di-iodide was prepared by passing acetylene over iodine moistened with alcohol (Sabanejeff, *Annalen*, 178, 109). The absorption is very slow. On removing the iodine a semi-fluid mass was obtained, which, when crystallised from alcohol, yielded long elastic needles of the di-iodide, melting at 73° . This body is remarkably

stable, and may be distilled without decomposition. Boiling point 192° (corr.). On distilling the alcoholic mother-liquor, a further portion of the solid iodide volatilised, together with some iodoform, and the residue, when precipitated with water, yielded a small quantity of the liquid isomeric iodide described by Sabanejeff. It solidified readily in ice.

Acetylene Chloriodide.

Acetylene chloriodide, C_2H_2ClI , may be prepared in the same way as the corresponding ethylene compound, obtained by Maxwell Simpson (*Proc. Roy. Soc.*, **11**, 590; **12**, 278), but the absorption of acetylene by a solution of iodine monochloride in hydrochloric acid, is by no means rapid, and must be aided by continual shaking. The solution of iodine chloride was prepared by passing chlorine over iodine until liquefaction had taken place, dissolving the product in four or five times its volume of hydrochloric acid, and treating the resulting brown solution with chlorine until it no longer lost colour.

The absorption-bottles were shaken up vigorously during the passage of the acetylene, and as soon as some quantity of the chloriodide had been formed, the absorption became tolerably complete. The crude chloriodide was washed, dried, and distilled. Between 117° — 120° about two-thirds of the liquid passed over; the thermometer then began to rise, and separation of iodine began. The residue could not be distilled without decomposition, even under greatly diminished pressure; neither was it possible to separate anything by means of a freezing mixture. On distilling at the ordinary pressure, much iodine was liberated, the thermometer rising gradually from 120° to 170° . Towards the end of the distillation, some fumes of hydriodic acid were noticed, and a small quantity of carbonaceous matter remained. The iodine was removed with thiosulphate, and the liquid was redistilled. By repeating this treatment a further considerable quantity of chloriodide was obtained, only a few drops of a higher boiling liquid remaining.

Possibly the compound $C_2H_2ClI_2$ is formed, and on distilling breaks up into C_2H_2ClI and I_2 . The chloriodide was obtained as a heavy liquid, becoming pink on exposure to light, with an odour like that of ethylene bromide. It boils at 119° (thermometer in vapour). Specific gravity at $0^{\circ} = 2.2298$.

Analysis gave the following results:—

0.4237 gram chloriodide yielded 0.8517 gram $AgI + AgCl$. Loss of weight on treatment with chlorine 0.2062 gram. Corresponding to—

	Found.	Calculated for C_2H_2ClI .
I	67.57	67.37
Cl	18.83	18.82
(ClI)	86.28	86.2

Treated with alcoholic potash acetylene chloriodide yields a gas which precipitates ammoniacal cuprous chloride.

Bromine displaces the iodine, yielding acetylene chlorobromide and other products.

Acetylene Chlorobromide.

When acetylene is passed through an aqueous solution of bromine chloride, an oil separates which begins to boil at about 130° , when some bromine is set free, and the temperature rises quickly to 230° , at which point most of the liquid distils over. Compounds containing more than two halogen-atoms are formed, and this is also the case when dilute solutions are employed.

As the chlorobromide was not to be obtained by direct combination, experiments were made with acetylene dibromide, which was heated with several metallic chlorides, but with a negative result.

Henry (*Ber.*, 3, 598) has prepared ethylene chlorobromide by treating the chloriodide with bromine (3—4 mols.), and this method was found to answer in case of the acetylene compound; only as the product is here unsaturated, bye-products are formed by addition of bromide and iodine. On adding bromine (2 mols.), drop by drop, to acetylene chloriodide under water, the mixture becomes dark, and much heat is evolved. If sodium thiosulphate is then added until the iodine, which at first precipitates, has redissolved, and the liquid is dried and distilled, pure chlorobromide passes over from 80 — 85° .

To obtain complete decomposition of the chloriodide, it is necessary to employ the bromine in the proportion of at least 2 mols. to 1 of chloriodide. The product of the reaction contains, besides the chlorobromide, at least two other bodies, richer in halogens. One of these begins to decompose, with separation of iodine and bromine, as soon as the thermometer reaches 90° . Efforts to isolate this substance by cooling the liquid in a freezing mixture, were unsuccessful, nothing separating out, and distillation with steam also failed to effect the purpose. It is possibly the compound C_2H_2ClBrI , for it decomposes on distillation, giving off iodine and bromine, and yielding a further quantity of chlorobromide, C_2H_2ClBr . The other addition-product distils over above 200° , and is a heavy oily liquid, smelling like acetylene tetrabromide; it is a chlorobromide, perhaps $C_2H_2ClBr_3$. The formation of these bye-products of course greatly diminishes the

yield of chlorobromide. In one experiment 20 grams of chloriodide were treated with 18 grams of bromine, and the mixture, after cooling, was left at rest for an hour. After removing the halogens with thio-sulphate, the product weighed 25 grams. On distilling, some chlorobromide was separated between $80-90^{\circ}$, and the thermometer then rose gradually to 190° , when the separation of iodine and bromine ceased. The distillate $90-190^{\circ}$ was then twice redistilled and treated with thiosulphate; it yielded, on fractionation, a further quantity of chlorobromide, making the total amount obtained 5 grams.

Analysis gave the following results:—

- I. 0.4278 gram substance decomposed with nitric acid and silver nitrate yielded 1.0016 gram mixed silver salts.
- II. 0.3497 gram gave 0.8236 gram silver salts. Loss of weight after treatment with chlorine, 0.1097.
- III. 0.3539 gram gave 0.8318 gram silver salts. Loss of weight, 0.1101.

Corresponding to

	I.	II.	III.	Calculated for C_2H_3ClBr .
(ClBr)....	81.57	82.04	81.8	81.62
Br	—	56.39	55.92	56.53
Cl.....	—	25.47	25.63	25.09

Acetylene chlorobromide is a volatile liquid with a pleasant ethereal odour boiling at $81-82^{\circ}$. Sp. gr. at $0^{\circ} = 1.8157$.

It is isomeric with the chlorobromethylene obtained by Hugo Müller (this Journal, 1864, [ii], 420) by the action of potassium cyanide on chlorethylene bromide, and also by Denzel (*Liebig's Annalen*, 195, 206), who treated the same compound, C_2H_3ClBr , with alcoholic potash. The compound obtained by these chemists differs greatly from acetylene chlorobromide; it boils at 62° , has an excessively pungent odour, and polymerises with great ease. Its constitutional formula has been proved to be $CH_2 - CClBr$. The body described above must therefore possess the symmetric constitution $CHCl-CHBr$, as indeed might be expected from its mode of formation and boiling point.

Warmed with alcoholic soda, acetylene chlorobromide gives off a gas which explodes spontaneously, doubtless chloracetylene.

Acetylene Bromiodide.

This compound is formed, together with other products, on passing acetylene through an aqueous solution of bromine iodide.

The solution was prepared by treating iodine with bromine mixed

with four or five times its volume of water, warming the mixture, leaving it at rest, and pouring off from the excess of iodine. On passing acetylene through this solution, it was found that to obtain absorption, the bottles must be shaken continuously. As no convenient mechanical arrangement was at hand for the purpose, another plan was adopted. Several large bottles were fitted with stopcocks, some solution was placed in each, the air exhausted, and acetylene allowed to take its place. From time to time the bottles were shaken and connected with a supply of acetylene.

The black oil which separated was freed from iodine and bromine by washing it with thiosulphate solution. On distilling, it decomposed with separation of iodine; the same took place on exposure to light. Distillation in a current of steam, however, caused only a slight decomposition, the liquid becoming claret-coloured and a portion of it passing over with the greatest ease. There remained in the retort a reddish oil which refused to volatilise. Towards the end of the distillation, a small quantity of a crystalline substance came over, having the odour and properties of acetylene iodide.

The distillate was freed from iodine and fractionally distilled. After four distillations, it yielded the following chief fractions: 110–115° consisting of acetylene dibromide, 145–150° acetylene bromiodide, and a few drops, 160–190°, which solidified in ice, and contained free iodine and hydriodic acid. The fraction 145–150° distilled chiefly between 147–148°. Analysis gave the following results:—

0.3045 gram substance decomposed with nitric acid and silver nitrate yielded 0.5537 gram mixed silver salts. Loss of weight on treating with bromine vapour 0.0619 gram.

	Found.	Calculated for C_2H_2BrI .
(IBr)	88.97	88.8
I	54.91	54.50
Br	34.12	34.33

Acetylene bromiodide is a heavy colourless liquid which becomes red on exposure to light. Its specific gravity at 0° (when solid) is 2.750, and at 17.5° 2.6272. It boils without decomposition at 150° (corr.) and solidifies at about + 8°. Heated with alcoholic soda, it gives off a gas having the properties of bromacetylene.

The oily liquid which remained after distilling off the bromiodide and other products in a current of steam, became claret-red on standing; it refused to solidify or deposit anything at – 12°. On distillation, it decomposed, with separation of iodine and bromine, leaving some carbonaceous matter, and the distillate was found to consist of acetylene dibromide, which is easily volatile with steam, and therefore

could not have existed as such in the original liquid. Analysis of the original liquid gave iodine 36 per cent., bromine 56 per cent., or about two equivalents of iodine to five of bromine. These numbers approach those required for the formula $C_2H_2Br_3I$, which requires iodine 32.3 per cent., bromine 61 per cent. The decomposition noticed makes it probable that the liquid in question consists mainly of a bromiodide of this formula.

The following table contains the boiling points and specific gravities of the halogen-derivatives of acetylene described in this paper, and of the isomeric substituted ethylenes; on the opposite side are the corresponding ethylene and ethylidene compounds. It will be seen that the boiling points of the mixed halogen-compounds of acetylene in each case lie midway between those of the corresponding simple derivatives. This being also true of the ethylene-compounds (Henry) one may calculate the boiling point of ethylene iodide as 197° , which differs from that of acetylene iodide by 5° . Taking the middle column of differences of boiling point, corresponding to H_2 , and regarding only the symmetric compounds, the differences augment as the molecular weights diminish, from five in the case of iodides to thirty in that of the chlorides. This does not appear to be the case with the dissymmetric compounds. As would be expected, the specific gravities of the acetylene derivatives are slightly greater than those of the corresponding ethylene derivatives.

The experiments described in this paper were made in the laboratory of University College, London.

TABLE.

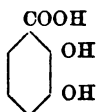
Diff.	Formula.	Sp. Gr.	B. P.	Diff.	B. P.	Sp. Gr.	Formula.	Diff.
—	$C_2H_2I_2$	3.803 at 21°	192°	—	dec.	—	$C_2H_4I_2$	—
—	$C_2H_2I_2$ (?)	2.942 " 21°	—	—	179-80°	2.84 at 0°	$C_2H_4I_2$	—
—	C_2H_2BrI	2.75 " 0°	150°	12	163°	2.516 " 29°	C_2H_4BrI	20°
—	C_2H_2BrI	—	—	—	142°	2.452 " 16°	C_2H_4BrI	
—	C_2H_2ClI	2.23 at 0°	119°	22	141°	2.151 " 0°	C_2H_4ClI	23°
—	C_2H_2ClI	—	—	—	118°	2.054 " 19°	C_2H_4ClI	
19°	$C_2H_2Br_2$	2.268 at 0°	110°	21	131°	2.163 at 21°	$C_2H_4Br_2$	19°
	$C_2H_2Br_2$	—	91°	19	110°	—	$C_2H_4Br_2$	
20°	C_2H_2BrCl	1.8157 at 0°	81-2°	26	108°	1.70 at 10°	C_2H_4ClBr	23°
	C_2H_2BrCl	—	62°	23	85°	1.667 " 16°	C_2H_4ClBr	
18°	C_2H_2Cl	—	55°	30	85°	1.271 " 0°	$C_2H_4Cl_2$	27°
	C_2H_2Cl	—	37°	21	58°	1.198 " ?	$C_2H_4Cl_2$	

In each pair of isomerides the symmetric compound is placed first.

LXII.—On Dihydroxybenzoic Acids and Iodosalicylic Acids.

By ALEX. K. MILLER, Ph.D.

OF the six acids of the formula $C_6H_3(OH)_2COOH$ theoretically possible, five are already known, and it was with the view of completing the series that the following research was undertaken. The acid remaining as yet undescribed is that represented by the formula—

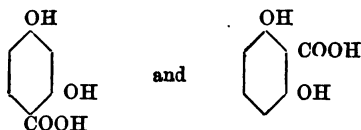


and may be conveniently termed *catechol-orthocarboxylic acid*.

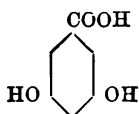
In order to prepare this acid I have tried two different methods, in the one case starting from catechol (pyrocatechin), and in the other from salicylic acid. It is evident that if the same acid should be formed, both by the introduction of a carboxyl group into catechol, and by replacing a hydrogen-atom in salicylic acid by hydroxyl, this acid must necessarily have the structure represented by the above formula.

Preparation of Dihydroxybenzoic Acids from Catechol.

In order to prepare dihydroxybenzoic acids from catechol, the method described by Senhofer and Brunner for the direct introduction of carboxyl into phenols, &c. (*Wien. Akad. Ber.*, 1879, 2 Abth., 504), was made use of. According to this method a phenol is heated in sealed tubes for several hours to a temperature of about 110° with a concentrated solution of ammonium carbonate. In this way Senhofer and Brunner obtained from resorcinol the following two dihydroxybenzoic acids:—



In the first of these two acids the carboxyl takes up the ortho- and para-positions respectively to the two hydroxyl groups, and in the second acid the ortho-position to both hydroxyl groups. The symmetrical acid—



was not formed in the reaction.

Starting from catechol there are only two dihydroxybenzoic

acids possible, namely, protocatechuic acid, $\begin{array}{c} \text{OH} \\ | \\ \text{C}_6\text{H}_2 \\ | \\ \text{COOH} \end{array}$, and the acid

$\begin{array}{c} \text{OH} \\ | \\ \text{C}_6\text{H}_2 \\ | \\ \text{COOH} \end{array}$, and since in the former the carboxyl is in the para-

position to one of the hydroxyl groups, and in the latter in the ortho-position to a hydroxyl group, it was thought possible that both acids might be formed. The experiment was carried out as follows:—

1 part catechol, 4 parts ammonium carbonate, and 5 parts water were heated in sealed tubes at a temperature of 130—140° for 14—16 hours. The tubes were then opened, and after nearly neutralising with hydrochloric acid, the liquid was filtered and the unaltered catechol extracted with ether. An excess of hydrochloric acid was then added to liberate any dihydroxybenzoic acid that might have been formed, and this was separated from the ammonium chloride by again shaking up with ether.

After evaporating the ether, a dark strongly acid residue was left behind, the weight of which amounted to about one-third that of the catechol employed. After repeated crystallisations from hot water, this residue was found to consist of two distinct acids, which had, however, been formed in very unequal proportions. One of these, which formed by far the greater part of the product, was found to be protocatechuic acid, as seen from the following properties:—It crystallised in needles and plates with 1 mol. of water of crystallisation, which it lost at 100°, and it melted at 199°. With lead acetate it gave in aqueous solution a white flocculent precipitate, and with ferric chloride an intense blue-green colour, which changed to red on the addition of sodium carbonate. On heating it with pumice-stone, carbonic anhydride was given off, and a sublimate of catechol was obtained. The catechol was recognised by the characteristic green colour which it gives with ferric chloride, changing to violet on addition of sodium carbonate; also by the precipitate which it gives with lead acetate. It melted at 100°.

The second dihydroxybenzoic acid was found in the mother-liquor from the protocatechuic acid. It had been formed only in minute

quantities, and could therefore not be obtained in the pure state or of constant melting point, this difficulty being further increased by its partial decomposition below the melting point. The highest melting point obtained was 192°.

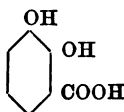
This acid differed from protocatechuic acid in its crystalline appearance and in its colour reaction with ferric chloride, producing a *pure blue* coloration which on addition of sodium carbonate changed to violet-red. By the slow evaporation of its solution in ether, the acid was obtained in nodules which presented an appearance totally distinct from that of the needles of protocatechuic acid.

On account of the very poor yield of the second acid only a single analysis could be made.

0.0979 gram substance gave 0.1980 gram CO₂ and 0.0375 gram H₂O.

Calculated for C ₇ H ₆ O ₄ .	Found.
C = 54.54 per cent.	55.15 per cent.
H = 3.90 ,,	4.25 ,,
O = 41.56 ,,	—
<hr/> 100.00	

Although the small quantity of this body which was at my disposal allowed so few experiments to be made, they are still sufficient to show that two dihydroxybenzoic acids can be obtained from catechol, one of which is protocatechuic acid. But since two only of these dihydroxy-acids can be derived from catechol, the only formula possible for the second acid is—



and that this constitution is the correct one is further confirmed by the experiments described below.

In the second method employed for obtaining the acid just mentioned, salicylic acid was submitted to the direct action of iodine, and the resulting iodosalicylic acids were converted into dihydroxybenzoic acids by melting with potash.

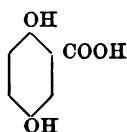
Although different chemists have already worked upon this reaction, the results obtained differ so much among themselves that it appeared desirable to repeat the investigation.

Lautemann (*Annalen*, 120, 301), for instance, prepared iodosalicylic acid by boiling a solution of salicylic acid and iodine in alcohol. The acid he obtained melted at 196°. On heating with potash it gave an oxyalicylic acid (*i.e.*, dihydroxybenzoic acid), which he characterised

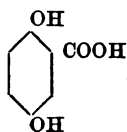
as follows:—It melted at 193° , crystallised anhydrous, and gave with ferric chloride a deep blue colour, changing to violet on addition of sodium carbonate. With acetate of lead a yellowish-white precipitate was produced. On heating his oxysalicylic acid with pumice-stone, Lautemann obtained a distillate which he found to be a mixture of catechol and quinol.

Liechti (*Annalen*, Suppl. 7, 133) made iodosalicylic acid by heating salicylic acid in aqueous solution with iodine and iodic acid. He gives 184° as the melting point of his acid. On melting his mono-iodosalicylic acid with potash, he obtained a dihydroxybenzoic acid which melted at 183° . Like Lautemann's acid, it gave a deep blue colour reaction with ferric chloride.

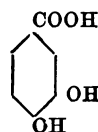
Demole (*Ber.*, 7, 1437) prepared iodosalicylic acid according to Liechti's method, and confirmed his melting point. He also converted the iodosalicylic acid into dihydroxybenzoic acid, and here again obtained the same results as Liechti. On heating his dihydroxybenzoic acid with pumice-stone, Demole obtained either pure quinol or a mixture of the latter with small and variable quantities of catechol. He says that more or less catechol is formed according to the temperature at which the acid is distilled, and that in some experiments he found scarcely any; so that since quinol is the chief and essential product of the reaction, it seems fair to suppose that Demole and also Liechti were dealing with quinolcarboxylic acid:



Demole examined further the action of melted potash on di-iodosalicylic acid, and, through the unexpected results which he obtained, he thought he could explain the discrepancies between his own and Lautemann's results. From pure di-iodosalicylic acid he obtained a mixture of two dihydroxybenzoic acids (instead of a trihydroxybenzoic acid as he expected) one of which was quinolcarboxylic acid,



, and the other protocatechuic acid,



Demole found further, that a mixture of moniodosalicylic acid with about $\frac{3}{4}$ di-iodosalicylic acid melted at 196° , i.e., at the same temperature which Lautemann gave for his moniodosalicylic acid, supposed to be pure. On melting this mixture with potash, Demole

obtained a mixture of quinolcarboxylic acid and protocatechuic acid, the latter resulting, as already mentioned, from the di-iodosalicylic acid. By the action of heat on these two dihydroxybenzoic acids, both gave off carbonic anhydride, the former yielding quinol and the latter catechol. In this way Demole tried to explain the high melting point of Lautemann's iodosalicylic acid and the fact of a considerable quantity of catechol being formed on heating his dihydroxybenzoic acid.

Goldberg (Dissertation, Würzburg, 1878) prepared iodosalicylic acid from salicylic acid by means of the diazo-compound. His acid also melted at 196° , and yielded a dihydroxybenzoic acid of melting point 197° , by the dry distillation of which Goldberg obtained pure quinol, so that there can be no doubt that he really had pure quinolcarboxylic acid. The acid is characterised by giving a deep blue colour-reaction with ferric chloride, also by *not* being precipitated by acetate of lead.

Although the iodosalicylic acids of Lautemann and Goldberg agree in melting point, important differences are found in the dihydroxyacids obtained from them and in the products of their decomposition, Lautemann's acid yielding principally catechol, which was, however, always accompanied by quinol, while Goldberg's acid yielded pure quinol.

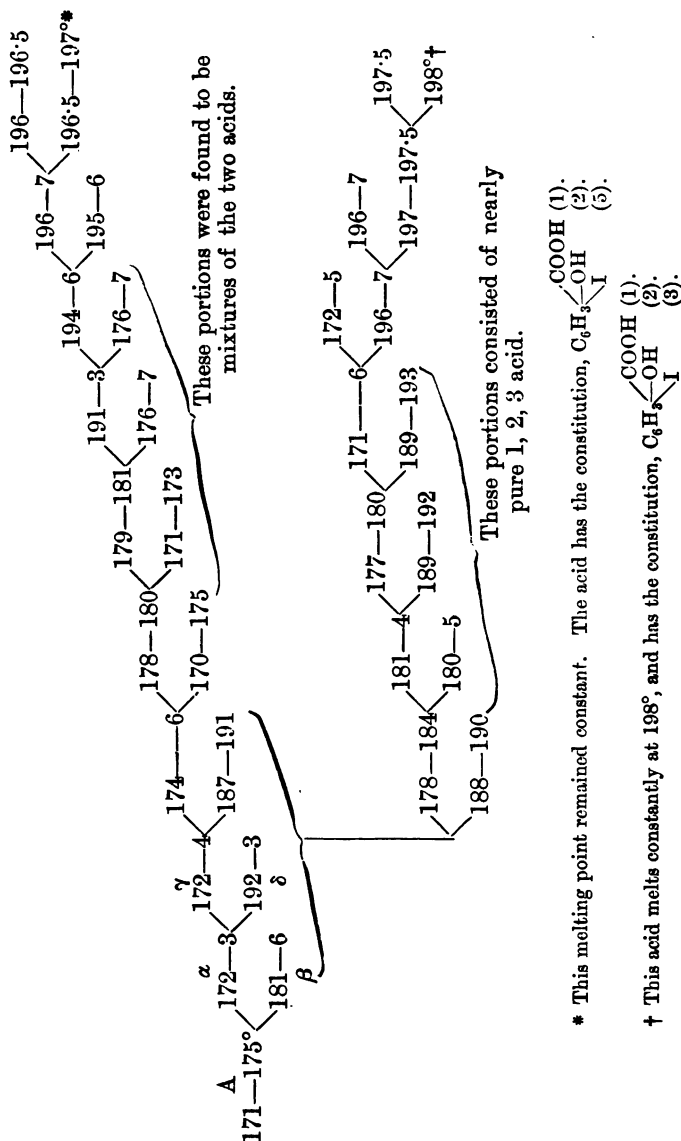
In order to decide whether Lautemann's acid was identical with Goldberg's, or with an isomeride having the same melting point, or, finally, a mixture of mono- and di-iodosalicylic acids as imagined by Demole, I have prepared iodosalicylic acid by Lautemann's method (see page 400).

For the separation of the mono- from the di-iodosalicylic acid and from unaltered salicylic acid, the mixture was boiled with water and barium carbonate, and the barium salts so obtained were repeatedly crystallised from hot water. In this way it is comparatively easy to obtain a product which analysis shows to be barium mono-iodosalicylate. That the same was, however, not a definite body was shown by the fact that the products of different preparations had different melting points; also that in recrystallising the barium salts, the iodosalicylic acid, separated from different fractions, showed the same chemical composition, though different melting points. Finally, this method had to be given up, and the attempt was made to get a pure product by crystallising the acid itself from water. Although on account of the very slight solubility of iodosalicylic acid in water, this method has the disadvantage that large quantities of liquid have to be employed, it seems to be the best for the separation of the isomeric acids.

In preparing iodosalicylic acid by Lautemann's method, two isomeric acids are in fact formed which melt at nearly the same temperature.

They differ, however, in crystalline appearance and in their solubility in water, and yield on melting with potash two different dihydroxybenzoic acids, as will be seen below.

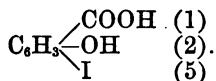
The separation and purification of these two iodosalicylic acids was systematically carried out as shown in the following scheme :—



This scheme represents, by way of example, a small part of that made up in the course of the work, which is much too lengthy and complicated to reproduce in full. The portion communicated will suffice to show to some extent the difficulty of separating the two acids.

The following short explanation will serve to make this scheme intelligible:—A small fraction of the whole iodosalicylic acid mixture A (melting at 171—175°) was dissolved in hot water. The crystals α (melting at 172—173°) separated out on cooling, while the evaporated mother-liquor yielded the crystals β (melting at 181—186°). By the further treatment of α , in the same fashion γ and δ were obtained, &c., &c., the final result being two crops of constant melting point, the more difficultly soluble acid melting at 197°, and the more easily soluble at 198°.

The former acid (197° m. p.) is identical, as will be hereafter shown, with that obtained by Goldberg. It is para-iodosalicylic acid, and has the constitution—



It crystallises from water in splendid long needles. Its solution gives a violet coloration with ferric chloride.

On analysis the following numbers were obtained:—

Calculated for	Found.
$\text{C}_6\text{H}_3\text{I}(\text{OH}).\text{COOH}.$	
C = 31.82 per cent.	31.68 per cent.
H = 1.89 ,,	1.92 ,,
I = 48.10 ,,	48.12 ,,
O = 18.19 ,,	

The barium salt of this para-iodosalicylic acid, obtained by boiling its aqueous solution with barium carbonate, crystallises with 4 mols. of water of crystallisation in warty conglomerations of scales. The dry salt requires for solution 120—125 parts water at 8°.

Conversion of Para-iodosalicylic Acid into Dihydroxybenzoic Acid.

The moist iodosalicylic acid was heated with an excess of potash till decomposition was complete. This was ascertained by acidulating a small portion with hydrochloric acid, which produced a precipitate so long as iodosalicylic acid remained undecomposed. The alkaline mass was left to cool, dissolved in water, and treated with an excess of hydrochloric acid, and the liberated dihydroxybenzoic acid was then separated by shaking out with ether. On evaporating the ethereal

solution, a brown residue was obtained, which was purified by crystallisation from water. The acid crystallises in anhydrous needles. Its aqueous solution gives with acetate of lead *no* precipitate, with ferric chloride a deep blue coloration, changing to red on addition of sodium carbonate. This red colour is, however, very unstable, and is at once destroyed by an excess of the reagent.

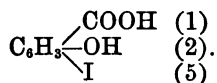
The acid melts at 200° , i.e., 3° higher than the melting point given by Goldberg. There can, however, be no doubt that the two are identical, and it may here be said that, for recognising the different isomeric dihydroxybenzoic acids, the melting points cannot well be depended upon, first, because most of these acids melt at temperatures very close to one another; and secondly, because they for the most part begin to decompose, either on melting or below their melting points, into carbonic anhydride and dihydroxybenzene.

In order better to establish the constitution of this acid and its identity with that of Goldberg, it was cautiously heated in an oil-bath to a temperature of 215° . Carbonic anhydride was given off, and a sublimate obtained of pure quinol, which was identified by its melting point (169°), and by its yielding the powerful and highly characteristic odour of quinone when warmed with ferric chloride. The absence of catechol was proved by the fact of lead acetate giving no precipitate. The barium salt of this dihydroxybenzoic acid crystallised in rosette-like groups, as described by Goldberg. In water it is very soluble, 1 part of salt requiring only 2.5 parts of water.

On analysing the acid the following numbers were obtained :—

Calculated for $C_6H_3(OH)_2.COOH.$	Found.
C = 54.54 per cent.	54.96 per cent.
H = 3.90 ,,	4.19 ,,

From the undoubted constitution of this quinolcarboxylic acid it is evident that the iodosalicylic acid from which it was obtained is also identical with that prepared by Goldberg, and that it has the constitution—



The second or more easily soluble iodosalicylic acid, obtained by the scheme of crystallisation referred to above (page 403), separated from its hot aqueous solution usually as an indistinct crystalline mass, but could be obtained by very slow cooling in well-formed needles, which, however, have a very different crystalline appearance from those of para-iodosalicylic acid. It will be shown to be the ortho-iodosalicylic acid sought after.

This acid melts at 198° , *i.e.*, one degree higher than the para-iodo-salicylic acid. Both give a violet colour-reaction with ferric chloride.

On analysis the following results were obtained :—

Calculated for $C_6H_3I(OH).COOH$.	Found.
C = 31.82 per cent.	31.91 per cent.
H = 1.89 ,,	1.89 ,,
I = 48.10 ,,	47.98 ,,
O = 18.19 ,,	

For the readier comparison of the two isomeric iodosalicylic acids, the barium salt of the last described acid was also made (see page 404). At 8° it requires for solution 190 times its weight of water, and is consequently much less soluble than the para-compound. It crystallises with $3\frac{1}{2}$ mols. of water in concentrically grouped needles.

On melting this second iodo-salicylic acid (ortho-iodosalicylic acid) with potash, a dihydroxybenzoic acid was obtained, which by its colour reaction with ferric chloride, could be easily mistaken for quinolcarboxylic acid, but by its other properties was shown to be a distinct acid. Ferric chloride produced a deep blue colour, which changed to violet-red on addition of sodium carbonate. This last colour is, however, distinguished from that which quinolcarboxylic acid gives, by not being destroyed by an excess of the sodic solution.

This new dihydroxybenzoic acid differs further from quinolcarboxylic acid in its crystalline appearance, and by sometimes containing water of crystallisation; also by giving a precipitate with acetate of lead, and by yielding on heating, carbonic anhydride and catechol. From water it crystallises either in anhydrous warty masses, or in well-formed needles with 2 mols. of water.

On analysis the following numbers were obtained :—

Calculated for $C_7H_6O_4$.	Found.
C = 54.54 per cent.	54.70 per cent.
H = 3.90 ,,	4.28 ,,

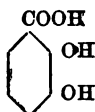
By the slow evaporation of an ethereal solution of this acid, it was obtained in small nodules which had exactly the appearance of the acid obtained from catechol and ammonium carbonate (see page 399). The two are in fact identical; with ferric chloride and sodium carbonate they both give exactly the same colour reactions; both give white precipitates with lead acetate, and both decompose on heating into carbonic anhydride and catechol. The acid melts at 204° .

In order to determine the temperature at which decomposition commences, the acid was mixed with powdered pumice and gradually

heated in an oil-bath, a slow current of carbonic anhydride being at the same time passed through the retort in which the mixture was contained. A sublimate of catechol began to be formed when the temperature had risen to 160—170°. This was resublimed between watch-glasses to free it from traces of undecomposed acid, and was then found to consist of pure catechol. It melted at 102—103°, gave the characteristic green coloration with ferric chloride, the colour changing to violet-red on adding sodium carbonate. With lead acetate it gave a white precipitate.

The barium salt of this dihydroxybenzoic acid crystallises in small transparent well formed prisms which are difficultly soluble in cold water, one part of the salt requiring at 18° 95—100 parts water. The salt crystallises with 5 mols. of water.

The fact that the above dihydroxybenzoic acid prepared from salicylic acid yields catechol on heating, is of itself proof that this acid must have the constitution



But this constitution is also the only one possible for the acid which was obtained together with protocatechuic acid by the introduction of a carboxyl-group into catechol (page 398). And since both of these methods have yielded one and the same product, there cannot be the least doubt as to its constitution.

Since in preparing the iodosalicylic acids, Lautemann's instructions have been followed, it is in the highest degree probable that Lautemann was also dealing with a mixture of two isomerides. On fusing with potash he would, in this case, naturally have got a mixture of the two dihydroxybenzoic acids. In this way it is easy to explain how the distillate from his dihydroxybenzoic acids contained both catechol and quinol, instead of assuming, as Demole did, that Lautemann's mono-iodosalicylic acid consisted principally of di-iodosalicylic acid.

The low melting points of Liechti's and Demole's iodosalicylic and dihydroxybenzoic acids, and the formation of small quantities of catechol by the distillation of the latter acid, may also perhaps find their true explanation in the assumption that the acids prepared by Liechti and Demole also contained small quantities of the isomeric ortho-acid.

The series of the six dihydroxybenzoic acids being now complete, I have compiled for comparison a table (pp. 409, 410) showing their principal properties, methods of preparation, &c.

The readiness with which these acids split up on heating seems to be connected with the relative positions of the carboxyl- and hy-

droxyl-groups to one another. It will be seen for instance that the acid which most easily gives off carbonic anhydride is the one in which the two hydroxyl-groups are in the ortho-position to the carboxyl-group. Then follow the acids in which the carboxyl is in the ortho-position to only one hydroxyl-group, and last of all the most difficultly decomposable symmetrical acid.

It will also be seen from the table that the solubility or insolubility of the lead compounds of these acids depends upon the relative position of the two hydroxyl-groups to one another. Of the three phenols, $C_6H_4(OH)_2$, catechol alone gives a precipitate with lead acetate, and of the six acids, $C_6H_3(OH)_2.COOH$, none yield precipitates with acetate of lead, except the two which are obtained from catechol.

In conclusion, I beg to thank Professor Wislicenus, in whose laboratory this research was carried out, for valuable advice and assistance received during the progress of the investigation.

TABLE OF THE DIHYDROXYBENZOIC ACIDS.

Constitution (COOH in 1).	Prepared		Crystalline form and water of crystallisa- tion.	Melting point.	Reaction with Fe_2Cl_6 .	Solubility.	Dry distil- lation.	With acetate of lead.	Ba-salt.
	By	From							
1, 2, 3 ortho-car- boxylic acid.	Catechol- Author.	Catechol and ammonic carbonate. Iodosalicylic acid.	Wart-like groups (an- hydrous). Needles with $2\text{H}_2\text{O}$.	204°C , de- composes	Deep blue coloration, which, with CO_3Na_2 changes to violet-red. The colour is not de- stroyed by excess of re- agent.	In cold water moderately soluble. In hot water, in alcohol and ether, easily soluble.	From $160-170^\circ$ decom- poses into CO_2 and catechol.	Flocculent precipi- tate.	Difficultly soluble prisms with 5 mols. H_2O .
	Brunner and Senhofer.	Resorcinol and ammo- nic carbon- ate.	Needles and plates with $\frac{1}{2}$, 1 $\frac{1}{2}$, or $3\text{H}_2\text{O}$.	$194-200^\circ$ decomposes. $204-206^\circ$, according to Tiemann.	Red colour.	In cold water difficultly, in hot water, alcohol, and ether, easily soluble.	From $160-168^\circ$ splits up into CO_2 and resor- cinol.	No preci- pitate.	Columnar crystals with $4\text{H}_2\text{O}$.
	Asher. Blomstrand. Tiemann and Parristius.	<i>p</i> -Cresolsul- phonic acid. Toluoldisul- phonic acid. Umbellife- rone.							
1, 2, 4 dihydroxyben- zoic acid.	Liechti, De- mole, Gold- berg, Author. Rakowski and Leppert. Senhofer and Sarley.	Iodosalicylic acid. Bromsalicylic acid. Quinol and KHCO_3 .	Anhydrous needles and prisms.	197° accord- ing to Rakowski and Gold- berg. 200° accord- ing to Author.	Deep blue colour, which changes to dirty red. with CO_3Na_2 , the colour being destroyed by an excess.	Easily solu- ble in water, alcohol, and ether.	Decom- poses into CO_2 and quinol.	No preci- pitate.	Rosette- like groups of needles.
1, 2, 5, trihydroxyben- zoic acid.									

TABLE OF THE DIHYDROXYBENZOIC ACIDS.

Constitution (COOH in 1).	Prepared		Crystalline form and water of crystallisa- tion.	Melting point.	Reaction with Fe_2Cl_6 .	Solubility.	Dry distil- lation.	With acetate of lead.	Ba-salt.
	By	From							
1, 2, 6 β -Dihy- droxyben- zoic acid.	Senhofer and Brunner.	Resorcinol and ammo- nic carbon- ate.	Long needles with 1 mol. H_2O .	148—167°; decomposes.	When di- lute, violet; concentra- ted, intense blue coloration.	Easily solu- ble in hot water; less in cold.	From 135° decom- poses into CO_2 and resorci- nol.	No preci- pitate.	Short, hard prisms, difficultly soluble in cold water. Crystal- lises with 1 mol. H_2O .
	Barth.	Bromanisic acid.							
1, 3, 4 Protoca- technic acid.	Malin.	Iodo- <i>p</i> -hy- droxyben- zoic acid.	Needles and plates with 1 mol. H_2O .	199°.	Blue-green coloration, changing to red on addi- tion of CO_2 and Na_2S .	Easily solu- ble in hot water, in alcohol, and ether.	Splits up into CO_2 and cate- chol.	Flocculent precipi- tate.	Crystallises with 5 mols. H_2O .
	Author.	Sulphanisic acid.							
1, 3, 5 Symmetri- cal dihy- droxyben- zoic acid.	Barth and Senhofer.	Catechol and ammonium carbonate.	Prisms and needles.	232—233°.	No coloration.	Moderately soluble in cold water; easily in hot water, in alcohol, and ether.	Heated with soda to 350° decom- poses into CO_2 and resorci- nol.	No preci- pitate.	Crystallises in wat- er-like groups with $4\text{H}_2\text{O}$.
		Disulphoben- zoic acid.							

LXIII.—*Crystalline Molecular Compounds of Naphthalene and Benzene with Antimony Trichloride.*

By WATSON SMITH and G. W. DAVIS.

It was observed by one of us some time ago (this Journal, June, 1879) that on melting a mixture of antimony trichloride and naphthalene, after removing the source of heat, a beautiful crystallisation commences in the still liquid mass, the minute but perfectly symmetrical clinorhombic tables in their rapid growth performing during the process singular gyrations upon the liquid surface on which they float.

Although these crystals are formed with great facility, it is no easy matter to separate them perfectly from the melted mixture in which they float, owing to the rapidity with which, on removal of the crystals, the adhering fluid solidifies upon them. This must be rapidly performed with a small platinum spatula, previously warmed.

It was found best to adopt the proportions by weight of 3 parts of antimony trichloride to 2 of naphthalene. The crystals on removal from the melted fluid in which they float must be at once placed in a dry stoppered bottle, as they are very deliquescent. Immediately on removal they are observed to be transparent, but a few moments later become whitish and opaque. They form perfect clinorhombic tables, and on analysis gave the following numbers :—

0.5425 gram gave 0.293 gram Sb_2S_3 = 0.2093 Sb = 38.58 per cent.
 0.4990 " 0.269 " Sb_2S_3 = 0.1914 Sb = 38.56 "

	Calculated for $3\text{SbCl}_3 \cdot 2\text{C}_{10}\text{H}_8$ per cent.	Found per cent.
Sb.....	38.94	(i) 38.58
		(ii) 38.56

Molecular Compound of Benzene with Antimony Trichloride.

Crystallised antimony trichloride is dissolved in benzene, so as to give a concentrated solution. It is best to take about 3 parts of the former to 4 of the latter. Solution may be promoted by gentle warming in a small flask, which is afterwards loosely corked, and then set aside for a few days. Large well-defined clinorhombic plates, much thinner and also more irregular than the naphthalene compound, are formed. They are perfectly colourless and transparent, and permanently so, thus differing from the naphthalene compound. They are also exceedingly deliquescent. Analytical numbers as follows were obtained :—

Weight taken = 0.594 gram.

Antimony trisulphide obtained = 0.3615 gram = 0.2582 gram Sb.
= 43.46 per cent.

A chlorine determination gave 37.62 . . .

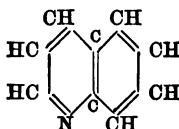
Calculated for 3SbCl ₅ .2C ₆ H ₆ per cent.	Found per cent.
Sb = 43.57	43.46
Cl = 37.90	37.62

LXIV.—*An Additional Evidence, by Analysis of the Quinoline Molecule, that this Base belongs to the Aromatic Series of Organic Substances.*

By WATSON SMITH and G. W. DAVIS.

MERZ, in conjunction with Ruoff, Moe, Zetter (*Inaug. Disserts.*), and other pupils of his, showed that on exhaustive perchlorination, all members of the aromatic series break up so as to yield perchlorobenzene, unaccompanied or accompanied with perchlorinated paraffin groups according to circumstances. An exception occurs in the case of diphenyl, which forms perchlorodiphenyl, and this body refused to disintegrate on further chlorination. The formation of perchlorodiphenyl was found to be of very rare occurrence. Of course in many cases the formation and separation of perchlorobenzene made it possible to predict what the perchlorinated members of the paraffin group formed at the same time in the general disintegration of the aromatic molecule must be. Thus light was obtained and thrown upon the constitution of several aromatic compounds, besides which a remarkable confirmation of the truth lying at the root of Kekulé's benzene-ring hypothesis was obtained.

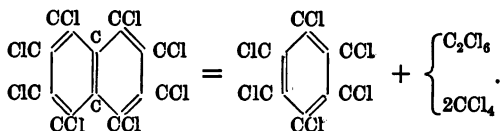
If quinoline has the constitution now generally assigned to it—



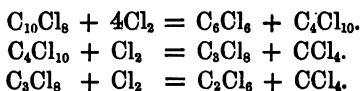
(and this has been made clear to a considerable extent by the several researches of Dewar, Baeyer, Königs, and Skraup), then by an exhaustive perchlorination according to the method of V. Merz, it might be expected that in the disintegration following, that portion of

the compound nucleus containing nitrogen would prove least stable as being most complex, and would consequently give way, yielding perchlorethane, perchloromethane, and nitrogen, whilst the other portion would yield perchlorobenzene.

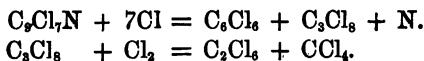
It will now be interesting to examine what the actual experience of Merz and Ruoff was in their perchlorination of naphthalene. They found that on repeated treatment in sealed tubes with antimony pentachloride at gradually increased temperatures, finally at 350° to about 400° C., naphthalene first changes to perchloronaphthalene, becomes disintegrated gradually and yields perchlorobenzene, perchlorethane, and perchlormethane,



This reaction, as regards the appearance both of perchlor-methane and -ethane, is better interpreted by assuming, as Graebe proposes, the presence in the naphthalene molecule of the group $(\text{C}_4\text{H}_4)''$, which becomes split off from the chlorinated benzene-ring as the first step of disintegration, and by the action of the chlorine is converted into perchlorbutane, which then immediately after its formation (as Krafft and Merz (*Ber.*, 1875, 1300) have actually shown in the case of perchlorbutane) at the high temperature, is first broken up into perchlorpropane and perchlormethane, and the former later on into perchlorethane and perchlormethane, thus:—



In our experiments then we might expect to realise the following, possibly:—



Perchloronaphthalene has of course been prepared and studied by Berthelot and Jungfleisch (*Ann. Chim. Phys.* [4], 15, 331); perchlorquinoline has, so far as we are aware, not been prepared as yet.

We took 1·7 grams of chemically pure quinoline, and placed it in a strong tube of hard glass, together with ten times its weight of antimony pentachloride, slowly and cautiously added. The tube was well sealed up and heated to 170°, then to 280°, to 320°, and finally to 400° about, each for a space of five hours, leaving the contents to cool, and

opening the tube after each heating, to allow hydrochloric acid gas and nitrogen to escape. Dry chlorine gas was then passed into the brown mass for about 20 minutes, and the tube, after re-sealing, was again heated at the above intervals as before. The chlorinating and heating were repeated till on opening the tube no more hydrogen chloride was evolved. The contents of the tube were now quite black from separation of carbon, but the mass was also crystalline. This black mass was now washed out with strong hydrochloric acid into a beaker and washed by decantation several times with strong hydrochloric acid and afterwards with a strong tartaric acid solution, till a portion of the filtrate from the mass gave no longer a precipitate of antimony sulphide with H_2S . The residue, dried and a portion submitted to sublimation, yielded vapours having the characteristic camphor-like odour of perchlorethane, which condensed to small white needles having a melting point of 210° . Now the melting point of perchlorethane is 183° : hence probably this first crop was contaminated with some perchlorobenzene which melts at $220-223^\circ$. This crop first obtained was submitted to a careful re-sublimation, when a melting point in the crop now obtained was exactly 182° , the correct melting point of perchlorethane. After the perchlorethane was all sublimed and expelled from the black mass, the temperature was further raised, when, after some time long white needle-shaped crystals formed themselves on the surface of the dark mass in the sublimation apparatus. A quantity of these needles was carefully collected, and it was observed, on heating a portion of them, that the vapour possessed only an extremely faint odour, unlike that of the perchlorethane; in fact the vapour might be described as odourless. The melting point of these crystals was 223° , which is the correct melting point of perchlorobenzene.

Quinoline is a substance which is exhaustively perchlorinated with the greatest difficulty, and in future experiments we should recommend a 10-hours' heating at each successive temperature already mentioned. The opening of the sealed tubes is by no means unattended with danger, and, for the sake of safety, we should recommend that after heating and leaving it to cool, the tube should be opened by just allowing the drawn-out point to project from the oven, and then to let the flame of a lamp play upon it.

No perchlormethane could be detected, and this was probably owing to the volatility of the substance, by virtue of which it would be carried off in the violent rushes of gas ensuing on opening the tube from time to time. The danger of the operation of opening the tube indeed prevented any observations of the nature of gaseous bodies generated during the process from being made.

It may now just be pointed out how our experience just described

coincides with that of Dewar, who in 1877 obtained quinolinic acid (this Journal, 1881, p. 1044) ($C_6H_4(NH_2).CH_2.CO.COOH$) by the oxidation of quinoline, this acid on distilling with soda-lime yielding aniline ($C_6H_5.NH_2$). Dewar thus by an oxidation process obtains analytically proof of the aromatic nature of quinoline, actually getting the benzene-nucleus with the still adherent nitrogen, now in the form of an amido-group. We have succeeded in obtaining analytically by a chlorination process the perchlorinated benzene-nucleus (C_6Cl_6), together with half the remainder of the residue containing the nitrogen-atom, also as a perchlorinated group, viz., as perchlorethane (C_2Cl_4).

Writing quinoline as $\overbrace{C_6H_4.N : C_2H_2 : CH_2}$, we have obtained by chlori-
 groups, $\underbrace{C_6Cl_6}$ $\underbrace{C_2Cl_4}$ nation the following
 as perchlorinated products,
 whereas—

Dewar obtained $C_6H_5.NH_2$ (aniline) as the result of an oxidation process, followed by a distillation of the product with soda-lime.

LXV.—On Orcinol and some of the other Dihydroxytoluenes.

By R. H. C. NEVILLE and Dr. A. WINTHER.

VARIOUS considerations had some time since led us to consider it highly probable that orcinol was a dihydroxytoluene of the constitution 1 : 3 : 5, a supposition which has since been shown to be true by Tiemann and Streng (*Ber.*, 1881, 1999). In order to satisfy ourselves upon this point, and to ascertain if some practicable method for its artificial production could not be found, we undertook the research recorded in the present notes.

As we were endeavouring to obtain satisfactory proof of its exact constitution, we avoided all methods involving the fusion of a compound with a caustic alkali, as this method has in some cases been found to cause the hydroxyl-group to attach itself at a position in the benzene-nucleus different from that occupied by the halogen or other group which has been eliminated.

For this reason we started with the dinitrotoluene 1 : 3 : 5, which has been prepared by Staedel (*Ber.*, 1881, 902), from both dinitro-orthotoluidine and dinitro-paratoluidine. We prepared it from the latter.

As obtained by us it crystallised in bright yellow needles, melting at 92.4° .

Analysis.

Empl. 0.2503 gram; vol. N = 32.5 c.c.; $t = 11^{\circ}$; $b = 743.5 = 15.13$ per cent. N. Theory requires 15.38 per cent.

We obtained a yield of from 60 per cent. to 65 per cent. of the theoretical amount.

On dissolving the dinitrotoluene in an alcoholic solution of ammonium sulphide it gets warm, and the addition of water then causes the precipitation of an orange-red substance. This was dissolved in dilute hydrochloric acid, filtered, and reprecipitated by ammonia.

This nitrotoluidine crystallises from alcohol and ether in red-brown lancet-shaped needles. There is frequently mixed with it a lighter-coloured body which is less easily soluble in ether or dilute hydrochloric acid, and may modify the characteristics of the nitrotoluidine. The best method of purification appears to be to dissolve the nitrotoluidine in hydrochloric acid and leave it for 12–24 hours in a warm place, when a white precipitate gradually forms. This must be filtered out and the liquid again left, and the filtration repeated until no further precipitate separates on standing or warming.

This white substance melts at from 170 – 180° , and appears to be the result of imperfect reduction.

The purified solution will now give, by neutralisation with ammonia, a precipitate which should be washed, dried, and crystallised from ether or alcohol. We thus obtained it in thick needles melting at 98 – 98.4° . It is very easily soluble in ether, also in alcohol and benzene, and somewhat so in water.

The salts appear to dissolve freely in water only, in presence of an excess of acid.

The chloride appears to give up a portion of its acid on drying in the air or washing with ether.

Analysis.

Empl. 0.2893 gram; vol. N = 45.5 c.c.; $t = 13.2^{\circ}$; $b = 758.6 = 18.47$ per cent. N. Theory requires 18.42 per cent. N.

We obtained a yield equal to about 50 per cent. of the dinitrotoluene used.

The nitrotoluidine was now dissolved in a warm mixture of equal volumes of sulphuric acid and water, and cooled, whereupon the sulphate crystallised out. An aqueous solution of potassium nitrite was now gradually added until the sulphate was all redissolved. An equal volume of water was now added, and the mixture warmed, whereupon

the diazo-compound, was decomposed with evolution of gas, and nitro-cresol formed. This separated as a brown oil. This oil and the ethereal extract of the mother-liquid were boiled with water and filtered hot. By this means most of the pitch, &c., was left on the filter, and the filtrate, on cooling, gave thick bright yellow needles of nearly pure nitro-cresol. These were purified by crystallisation from benzene or water.

Thus obtained it crystallised in bright yellow needles or prisms, very soluble in ether or alcohol, less so in benzene, and still less in water, easily soluble with a dark yellow colour in alkalis or their carbonates. It does not distil with steam. When crystallised from benzene its melting point is $90-91^{\circ}$, but when crystallised from water, $60-62^{\circ}$. This arises from its crystallising with water, as will be seen below.

By heating to 100° a sample which melted at $60-62^{\circ}$, or by drying it over sulphuric acid, or by recrystallising it from ether or benzene, its melting point was raised to $90-91^{\circ}$. If this was left long in the open air it attracted moisture, and then again melted at $60-62^{\circ}$.

In order to determine the amount of water of crystallisation some was left over sulphuric acid for various times.

	Gram.	M. p.		Gram.	Per cent.	M. p.
Empl.	0.1549	$60-61^{\circ}$	left for 7 days	lost 0.0161	$= 10.39$	$81-86^{\circ}$
,,	0.5307	$60-61$,, 6	,, 0.0534	$= 10.06$	$81-85$
,,	0.3160	$61-62$,, 5	,, 0.0330	$= 10.44$	$87-89$

1 molecular proportion of water would amount to 10.52 per cent.

Analysis of some Crystallised from Benzene and then Dried over Sulphuric Acid.

Empl. 0.2171 gram; vol. N = 17.5 c.c.; $t = 12.5^{\circ}$; $b = 742.2 = 9.3$ per cent. N. Theory requires 9.15 per cent.

The yield was about 65 per cent. of the theoretical amount.

The nitro-cresol was now reduced with tin and hydrochloric acid; after removal of the tin the liquid was evaporated, during which process it turned brown. The crystalline chloride was washed with ether to remove unreduced nitro-cresol, and was then used for conversion into dihydroxytoluene.

The base itself was not isolated. In order to obtain dihydroxytoluene 1 : 3 : 5 from the chloride, 1 gram of this latter was dissolved in a hot mixture of 13 grams sulphuric acid with an equal volume of water, the solution was diluted with 100 grams of water, cooled by a freezing mixture, and a solution containing 0.6 gram of potassium nitrite added. The decomposition of the diazo-compound

thus formed commences between 30° and 50° . The liquid was warmed to expel all the gas and complete the decomposition; then filtered and extracted with ether.

In this way we obtained a red-brown oil, which was purified by frequent distillation and crystallisation from benzene or chloroform. Thus we obtained it from chloroform in glittering white leaves, and from benzene in long needles or prisms. After drying for 14 days over sulphuric acid it melted at $106-108^{\circ}$.

Analysis.

	H	C
Empl. 0.1653 H_2O = 0.0932 = 6.26 p. c.		
„ 0.1611 H_2O = 0.0911 = 6.28 „ CO_2 = 0.4007 = 67.83 p. c.		
Theory for $\text{C}_8\text{H}_8\text{CH}_3(\text{OH})_2$		
requires.....	= 6.45 „	67.74 „

The question now remained, was this identical with the orcinol obtained in other ways? We compared it in all its reactions (viz., ammonia and moist air, chloride of lime, ferric chloride, sodium hydrate in air, sodium hydrate in chloroform) with orcinol otherwise obtained, and found them all to agree perfectly, with the exception of the melting point.

Lamparter (*Jahresb.*, 1865, 589) gives as the melting point of anhydrous orcinol, obtained from lichens, 86° , and when crystallised from water, 58° . Vogt and Henniger (*Jahresb.*, 1872, 410) find for the melting point of the orcinol they obtained from chlorotoluene-sulphonic acid, 57.1° , when crystallised from water.

We examined some orcinol obtained from Messrs. Hopkin and Williams, and found that although it agreed in all other respects with the descriptions usually given of orcinol, yet that the melting point varied from 56° to 107° , accordingly as crystals or fine powders were taken, and according to whether the temperature was raised slowly or fast. It appears certain that by very slow raising of the temperature the combined water is driven off, and then the orcinol melts at the higher point.

In trying the dihydroxytoluene prepared by our method (when crystallised from water) we got sometimes from $54-56^{\circ}$, sometimes $54-105^{\circ}$.

By distilling the orcinol from Hopkin and Williams between two watch-glasses, and by fractionating the distillate by changing the upper glass, we got—

For 1st	distillate.	m. p.	$54-81.6^{\circ}$
„ 2nd	„	„	$82-83.0$
„ 3rd	„	„	$107-108.5$
„ 4th and 5th	„	„	$107-108.0$

Treating the substance obtained by us in a similar way we got—

For 1st distillate	m.p.	54—55°
„ 2nd	„	90—98
„ 3rd	„	98—103
„ 4th	„	97—104

It does not appear that by merely raising the temperature to 100° the whole of the water can be satisfactorily driven off.

On placing Messrs. Hopkin and Williams' orcinol in a partial vacuum over sulphuric acid, the melting point after 24 hours was—

	106·5—107·5°
After 8 days	106·5—108·0
and the same after 14 days.	

Our substance similarly treated gave, after

24 hours	m.p.	104—105°
After 8 days	„	105—107
„ 14	„	106—108

Some of Messrs. Hopkin and Williams' orcinol, which had been dried for 14 days, and which melted at 106·5—108°, was analysed—

Empl. 0·2261 gram; $\text{CO}_2 = 0·5561 = 67·08$ p.c. C. Theory = 67·74
 $\text{H}_2\text{O} = 0·1253 = 6·16$ „ H. „ = 6·45

It appears therefore certain that the dihydroxytoluene, 1 : 3 : 5, obtained in the manner we have described, is identical with orcinol.

The melting point of orcinol, when containing water, seems to be about 56°, but the actual point of complete fusion is very hard to determine. When the compound is anhydrous, or nearly so, the melting point seems to be 106·5—108°. It appears very hard to remove the last traces of water. Some orcinol from Messrs. Hopkin and Williams was placed *in vacuo* over sulphuric acid.

Empl. 0·3230 gram; after 45 hours it had lost 0·0254 = 7·86 per cent. (m.p. 106·5—107·5°).

5 days	„	„	0·0301 = 9·32 per cent.
12 „	„	„	0·0373 = 11·55 „
			(m.p. 106·5—108°).

Again—

Empl. 0·3496 gram; after 25 hours it had lost 0·0321 = 9·18 per cent.

10 days	„	„	0·0402 = 11·5 „
			(m.p. 107—108°).
12 „	„	„	0·0411 = 11·73 per cent.
			(m.p. 107—108°).

Theory for $\text{C}_6\text{H}_3\text{CH}_2(\text{OH})_2 + \text{H}_2\text{O}$ requires 12·67 per cent.

The artificially-prepared orcinol appears to behave in the same way.

Empl. 0.1 gram; after 4 days it had lost $0.0114 = 11.4$ per cent.

„ 12 „ „ $0.0125 = 12.5$ „

In further prosecution of our researches, we have succeeded in preparing orcinol by other methods, viz., from metabromo-toluene-metasulphonic acid. This was described by us in this Journal, 1880, 627, and *Ber.*, 1880, 1944—1948. By taking the potash salt of this and fusing it with twice its weight of caustic potash at a temperature of about $280-300^\circ$ for from half-an-hour to one hour, a mass was obtained which was dissolved in water and acidulated, extracted first with benzene to remove bye-products, and then with ether. The ethereal extract, on evaporation, left a brown oil, which, by distillation, gave a white distillate, slowly becoming crystalline. A fractional distillation of this substance, after crystallisation from water, gave distillates as follows:—

1st m. p.	54—56°
2nd „	54—100
3rd „	98—103
4th „	100—104

Some dried over sulphuric acid had the melting point $103-103^\circ$.

Analysis.

Theory for
 $C_6H_3CH_3(OH)_2$.

Empl. 0.1863 gram $H_2O = 0.1057 = 6.31$ per cent. H; 6.45 per cent.

$CO_2 = 0.4648 = 67.92$ „ C; 67.74 „

It gave all the reactions of orcinol with chloride of lime, ferric chloride, sodium hydrate and air, sodium hydrate and chloroform, and ammonia and moist air; and we may therefore conclude that it is identical with the above. We have also prepared orcinol from metabromometatoluidine (described by us in this Journal, 1880, 432).

We dissolved it in a warm mixture of equal volumes of sulphuric acid and water; on cooling, the sulphate crystallised out. A solution of potassium nitrite was now gradually added until the crystals were dissolved. Water was now added and the solution warmed, when gas was evolved and an oil separated out. This was purified by distillation with steam. The oil slowly solidifies into a mass of white crystals, which may be completely purified by solution in dilute caustic soda, filtration, short boiling, acidification, and then repeated distillations with steam. The boiling with caustic soda seems to drive off a substance, volatile with steam and insoluble in the soda. As the

substance is slightly soluble in water, the mother-liquids should be extracted with ether.

This substance melts at $56-57^{\circ}$, is very easily soluble in ether and alcohol, and somewhat in water.

Analysis.

Empl. 0.4120 gram; $\text{AgBr} = 0.4097 = 42.32$ per cent. Br. Theory requires 42.78 per cent. for monobromocresol.

The metabromo-metacresol thus obtained was heated to $280-300^{\circ}$ with twice its weight of caustic potash for one hour. The melt was acidified and extracted by ether. The ethereal extract was distilled, and in this way we obtained a distillate, solidifying into crystals, and possessing all the characteristics of orcinol.

Orcinol was also obtained from metadibromotoluene by heating it in a closed iron tube, with twice its weight of potassium hydrate, dissolved in a small quantity of water for two hours from $280-300^{\circ}$.

It was further obtained from toluene-metadisulphonic acid.

As a starting point, we took ortho-amido-toluene-metasulphonic acid, and heated 5 grams of it with 15 grams of strongly fuming sulphuric acid to $150-170^{\circ}$ for between half-an-hour and an hour.

The mass then dissolved easily in water, and was treated with barium carbonate to remove the excess of sulphuric acid. The barium salt filtered, a very small excess of sulphuric acid added to remove the barium, and the filtered solution evaporated to dryness and dissolved in alcohol, re-evaporated to dryness, and redissolved in alcohol and again evaporated. The mass thus obtained was very easily soluble in water or alcohol, but not in benzene.

Analysis.

Empl. 0.4720 gram; $\text{BaSO}_4 = 0.8234 = 59.89$ per cent. SO_3 . Theory for amido-toluol-disulphonic acid requires 59.92 per cent.

In a previous communication (this Journal, 1880, 625) we have pointed out that the sulpho-group in the monosulphonic acid occupies the position para to NH_2 and meta to CH_3 . In order to determine the position of the other sulpho-group, we converted the amido-sulphonic acid into a diazo-compound by introducing nitrous gas into a mixture of it with alcohol or benzene. The diazo-compound was boiled with water, a few drops of nitric acid then added, and the whole boiled until crystals appeared on cooling. These were filtered out, a few drops more nitric acid added, and the liquid boiled again, this operation being repeated as often as any further crop of crystals was obtained. In this manner six crops of crystals were obtained,

which all had the melting point 85° , and possessed all the properties of dinitroorthocresol.

Now this last has the two nitro-groups in the two positions meta to CH_3 , as was pointed out by us in a former communication (this Journal, 1880, 631), also by Staedel (*Ber.*, 1881, 901).^{*} Hence we conclude that the two sulpho-groups displaced by the nitro-groups had the same position, and that the acid thus obtained is ortho-amido-toluene-metadisulphonic acid. The para-amidotoluene-metadisulphonic acid may be obtained in an analogous manner. When the diazo-compound of either of these acids is heated with absolute alcohol under pressure, the toluene-metadisulphonic acid is formed. The solution is then evaporated, after neutralisation with an alkali or alkaline carbonate, and on heating the resulting salt with caustic alkali to from 200° to 300° , orcinol is produced, in all respects identical with that produced by the other methods described.

In pursuing these researches, we prepared also the dihydroxytoluene 1 : 2 : 4, proceeding as follows:—We start from ortho-nitro-para-toluidine (m. p. $77-78^{\circ}$). 40 grams of this was dissolved in 300 grams of a mixture of 1 vol. sulphuric acid with $1\frac{1}{2}$ vols. of water, and the solution cooled. This causes the separation of crystals of the sulphate.

A solution of potassium nitrite was now gradually added until all the crystals of sulphate were dissolved. It is best to add the potassium nitrite by a tube reaching to the bottom of the vessel. 3200 grams of a mixture of equal parts of sulphuric acid and water were now added, and the whole heated gradually until the evolution of gas ceased. On cooling, crystals of nitrocresol separated out. The mother-liquor was extracted with ether after the addition of water; and by evaporation of the ether a further quantity of nitrocresol was obtained. In this manner the total yield of nitrocresol reached about 80 per cent. of the theoretical quantity. In order to purify it, the ethereal solution was shaken with animal charcoal, or the nitrocresol was crystallised from water. By slow evaporation of an ethereal solution it was obtained in hard yellow prisms of m. p. $77-77.4^{\circ}$. It dissolves in alkalis and their carbonates with an orange-red colour, but the aqueous solutions of the salts partially decompose on heating. It is easily soluble in ether and alcohol.

Analysis.

Empl. 0.3313 gram; vol. N = 25.5 c.c.; $t = 8^{\circ}$; $b = 747.5$ mm.

N per cent. = 9.14. Theory for $\text{C}_6\text{H}_3\text{CH}_3\text{NO}_2\text{OH} = 9.15$.

^{*} We, in common with Nölting and Salis (*Ber.*, 1881, 982), found the melting point of pure dinitro-ortho-cresol higher than did Staedel, viz., 85.8° ; Nölting and Salis give 86° .

This nitrocresol is easily reduced by tin and hydrochloric acid. The solution may be freed from tin by hydrogen sulphide, and the filtered liquid evaporated to dryness. In this way a crystalline residue of chloride of amidocresol is obtained, but it is always coloured brown in the process of evaporation. Any unreduced nitrocresol remaining may be removed by washing with ether. The chloride is easily soluble in water, but on the addition of an alkali, or alkaline carbonate or ammonia, the liquid becomes brown or green.

In order to prepare from this the dihydroxytoluene 1 : 2 : 4, one gram of it was dissolved in 13 grams of a warm mixture of equal volumes of sulphuric acid and water. The mixture was now diluted with 100 grams of water, cooled by a freezing-mixture, and a dilute solution of potassium nitrite added until a slight smell of nitrous acid remained permanent; an excess of nitrite injures the reaction. The liquid was now warmed from 90° to 95°, filtered, and exhausted with ether. The ether by evaporation left a brown oil, which was boiled with benzene. The benzene was decanted off and distilled, and the residue remaining after the benzene had distilled off further distilled. In this way an oily distillate was obtained, which after some time crystallised. This was purified by frequent sublimations and crystallisations from benzene or toluene, and was thus eventually obtained of melting point 104–105°.

Analysis.

Empl. 0.0953 gram; $H_2O = 0.0566 = 6.61$ per cent. H.

$CO_2 = 0.2364 = 67.65$ „ C.

Theory for $C_8H_8, CH_3, (OH)_2$,

requires..... H = 6.45 per cent.

C = 67.74 „

The reactions agree pretty closely with those described by Håkanson (*Ber.*, 1872, 1087) for the dihydroxytoluene obtained by him from the toluenedisulphonic acid prepared from toluene and fuming sulphuric acid, and it is probable that they are identical.

Since this paper was written, Knecht (*Ber.*, 1882, 298) has obtained this dihydroxytoluene in a similar manner, and gives 103° as the melting point.

We have also prepared the dihydroxytoluene 1 : 2 : 5.

For this purpose we start from the nitro-orthotoluidine produced by the nitration of ortho-acetotoluid, and which we showed (this Journal, 1880, 436) had that constitution.

40 grams of metanitro-orthotoluidine (m. p. 127–129°) were dissolved in 300 grams of a warm mixture of equal volumes of sulphuric acid and water. The mixture cooled, and a solution of potassium nitrite carefully added until the crystals of sulphate

deposited on cooling were all dissolved. 1600 grams of a mixture of 1 vol. sulphuric acid to 2 vols. of water were then added, and the mixture gently warmed. The decomposition of the diazo-compound takes place at a temperature of 70—90°. A brown oil separates out which crystallises on cooling, and fine needles form in the liquid. These crystals and a further portion extracted from the mother-liquid with ether were dissolved in ether, and purified with animal charcoal.

Owing to the formation by the above process of dinitro-ortho cresol as well as mono-nitrocresol, the perfect isolation of the latter is difficult. We found that the best method was to dissolve the mixed cresols in potash solution, and separate the more from the less soluble portion. (The potassium salt of dinitro-orthocresol is much less soluble in cold potash-solution than the salt of the mono-nitrocresol). We then reprecipitated the cresol with sulphuric acid. By repeating these operations we got the compound tolerably pure.

The metanitro-orthocresol thus obtained crystallises from water in fine glittering bright yellow needles, melting at 30—34°; but by drying it on paper or on a water-bath, or by crystallising it from ether, its melting point is raised to 94·6—95°.

It is not freely soluble in water, but easily in alcohol or ether, and also in solutions of alkalis or their carbonates. The salts of the alkalis dissolve in water with an orange-yellow colour.

Analysis.

Empl. 0·2267 gram; vol. N = 17·5 c.c.; $t = 7·8^\circ$; $b = 750·3$ mm. = 9·02 per cent. N. Theory for $C_6H_3CH_3NO_2OH$ requires 9·15 per cent. N.

An easier way of obtaining the pure mononitrocresol was found to consist in boiling the metanitro-orthotoluidine with moderately concentrated solution of soda until it dissolved. In this way few, if any, bye-products, except a little pitch, seem to be formed. The pitch is easily removed by filtration, and by then precipitating the nitrocresol with sulphuric acid, extracting with ether and shaking with animal charcoal, it may be obtained at once nearly pure, and the yield is very nearly theoretical. The nitrocresol obtained in this manner presented exactly the same characteristics as that obtained in the other manner—

Analysis.

Empl. 0·2895 gram; vol. N = 23·25 c.c.; $t = 9·6^\circ$; $b = 757$ mm. = 9·60 per cent. N. Theory requires 9·15 per cent. N.

It appears from the above that the fluid nitro-orthocresol which Hofmann and Miller (*Ber.*, 1881, 571) consider to have the constitution 1 : 2 : 5 must have some other constitution.

The nitrocresol obtained by either of the above processes is easily reduced by tin and hydrochloric acid. After the tin has been removed by hydrogen sulphide, the chloride of the amidocresol is easily obtained by evaporation in good crystals coloured brown by the slight products of decomposition. These were washed with ether to free them from undecomposed nitrocresol.

The free amidocresol was not obtained, as it decomposed immediately on being set free from its salts, giving a greenish-yellow or red-brown colour to the solution from which ether extracted nothing but a red-brown pitch.

In order to obtain the dihydroxytoluene 1 : 2 : 5 the chloride of the amidocresol was dissolved in a considerable quantity of a very dilute sulphuric acid. To this was added a dilute solution of potassium nitrite until the smell of nitrous acid remained permanent for a short time. More water was then added, and the mixture boiled until all disengagement of gas ceased. The cooled and filtered liquid was then exhausted with ether. On evaporation, the ether gave red-brown crystals, which were purified by sublimation and recrystallisation from benzene in which they are not freely soluble. It was obtained from benzene, in white pearly leaves, melting at $124-125^{\circ}$, freely soluble in alcohol, ether, or water. From water it crystallises in colourless crystals, which melt at $123-125^{\circ}$, and do not appear to contain any water of crystallisation.

This dihydroxytoluene was prepared from the nitrocresol obtained from nitro-orthotoluidine by both the above-mentioned methods, and in both cases appeared identical.

Analysis.

Theory for
 $C_6H_3CH_3(OH)_2$
 requires

Empl. 0.2247 gram; $H_2O = 0.1480 = 7.31$ p. c. H. H = 6.45 p. c.
 $CO_2 = 0.5567 = 67.56$ „ C. C = 67.74 „

This dihydroxytoluene appears to be identical with the hydrotoluquinone of Nietzki (*Ber.*, 1877, 834) prepared from toluquinone from orthoamidoazotoluene. With soda-solution it gives a pretty blue-green colour, which very quickly turns to dark brown. With chloride of lime it turns blue-green, as with soda, then brown; but with a weak solution of chloride of lime a brownish-red. Chloroform and soda produce a brown colour; ferric chloride a brownish-red, or in a dilute solution, yellow. Ammonia in presence of moisture changes it into a dark brown mass, which dissolves in alkalis with a brown colour, and the addition of acetic acid to the solution causes the precipitation of brown flocks.

We also made some investigations into the preparation of hydroxy-toluene 1 : 3 : 4, starting from metanitroparatoluidine (m. p. 114—115°).

Armstrong and Thorpe (*Jahresb.*, 1876, 452) obtained, by nitration of paracresol, a nitrocresol identical with that which Wagner (*Ber.*, 1874, 537) obtained by heating metanitroparacetotoluid with sodium hydrate. This nitrocresol must have the required constitution, viz., 1 : 3 : 4, unless some molecular change takes place. Wagner by this method, however, obtained only small quantities. We therefore tried to prepare it from the diazo-compound, in the hopes of getting a better yield.

10 grams metanitroparatoluidine was dissolved in 100 grams of a mixture of equal parts of sulphuric acid and water, and a solution of potassium nitrite was added until a sample of the solution no longer gave a precipitate of nitrotoluidine on addition of water. The solution was then decomposed by heating, 800 grams of a mixture of 1 vol. sulphuric acid and $1\frac{1}{2}$ —2 vols. of water having first been added. The result, however, was unsatisfactory, as neither in the distillate nor in the ethereal extract was any large quantity of nitrocresol obtained, but only a very little melting at 33°.

We therefore tried Wagner's method, and after some experiments succeeded in getting a very good yield. The best plan is to take say 10 grams, and heat it with about 50—100 grams of a 20 per cent. solution of sodium hydrate for 15 hours; then pour off the liquid, and boil the remaining nitrotoluidine with a fresh charge of sodium hydrate, repeating this process until it is all dissolved. All the sodium hydrate liquors are then mixed, acidified with sulphuric acid, and distilled. In this way an almost theoretical yield is obtained; from 20 grams of nitrotoluidine we obtained 19 grams of nitrocresol. This good yield allows us to assume that no molecular change takes place, and that the nitrocresol has the constitution 1 : 3 : 4. The substance when purified was obtained from benzene in yellow crystals, melting at 33—33·4°, easily soluble in caustic alkalis, ether, or alcohol, but scarcely soluble in water. A portion of this nitrocresol was reduced by tin and hydrochloric acid. After removal of the tin by a current of hydrogen sulphide, the filtrate was evaporated to dryness. The chloride (1 gram), dissolved in 100 grams water and 13 grams sulphuric acid, cooled by a freezing mixture, and 0·6 gram of potassium nitrite in solution added. The solution was then warmed, filtered, and extracted with ether. An oil was thus obtained, which dissolved easily in water. The aqueous solution was coloured green by ferric chloride, on adding ammonia or sodium carbonate gradually the colour became first blue and then violet.

This oil is probably the dihydroxytoluene, 1 : 3 : 4. Its properties

coincide with those of homocatechol, which Tiemann (*Ber.*, 1877, 210; and 1878, 672) obtained by heating the calcium salt of alpha-homoprotocatechuic acid, and from coniferyl alcohol. They also regarded it as a dihydroxytoluene, 1:3:4.

It would appear from our investigations, as well as those of others, that inasmuch as orcinol evidently has the constitution 1:3:5, those reactions by which it has been obtained from substances of other constitution, such as chlorotoluene-sulphonic acid (1:2:4), must have involved a molecular change.

We subjoin a table of the reactions of the different dihydroxytoluenes above described. Circumstances have prevented us from investigating the dihydroxytoluene 1:3:4 as fully as we could have wished, as also the two others, viz., 1:2:3 and 1:2:6; but we hope to resume the investigation at some later date.

Reagent.	Orcinol, 1·3·5.	1·2·5.	1·2·4.	1·3·4.
Ammonia and damp air.	Intense red violet, diss. in alkalis with red-violet colour. Acetic acid precipitates red flocks.	Dark brown, dissolves in alkalis with brown colour. Acetic acid precipitates brown flocks.	Reddish, then brown, then green, then blue. Blue changing to red by addition of acetic acid, without any precipitation.	
Chloride of lime.	Deep violet-red, then brown and yellow.	Blue-green, then brown. When dilute, brownish-red.	Yellow.	
Ferric chloride.	Deep black-violet.	Brownish-red, yellow in dilute solutions.	Blue, scarcely changing.	Green; on gradual addition of NH_3 or Na_2CO_3 , became blue and then violet.
Sodium hydrate and air.	Red.	Pretty blue-green, changing to dark-brown.	Rose-red, then brownish.	
Chloroform and sodium hydrate on heating.	Red, after a while a green fluorescence, yellow by transmitted light.	Brown.	Rose-red.	

NOTE.

The above paper was written principally in the autumn of 1881, but its publication has been delayed, owing to our having applied for protection for the method of manufacturing orcinol, and since it was written, independent workers have published some of the above results. We have, however, thought it better to publish the paper in its entirety, at the risk of repeating work already done. We may perhaps take this opportunity of noticing a paper by C. Langer (*Ber.*, 1882, 1061—1065), on the law of substitution of aromatic amines, and point out that the law he there enunciates is really nothing else than the law which we showed to be true in a communication to this Society in 1880 (this Journal, 1880, 430), stated in other words.

P R O C E E D I N G S

A T T H E

M E E T I N G S O F T H E C H E M I C A L S O C I E T Y ,

S E S S I O N 1 8 8 1 - 8 2 .

November 3rd, 1881.

Dr. Gilbert, Vice-President, in the Chair.

The following papers were read :—

“On Citraconic and Mesaconic Ethers, and on Maleic and Fumaric Acids :” by W. H. Perkin.

“On the Action of Potassium Cyanide on Bismuthous Nitrate :” by M. M. P. Muir.

“On the Atomic Weight of Bismuth :” by M. M. P. Muir.

“Additional Observations on the Halogen Salts of Bismuth :” by M. M. P. Muir.

“Note on the Action of Sulphuric Acid on Zinc and Tin :” by M. M. P. Muir and C. E. Robbs.

“On the Volumetric Estimation of Bismuth in the Form of Oxalate :” by M. M. P. Muir and C. E. Robbs.

“Note on the Influence of Water on the Reaction between Potassium Iodide and Chlorine :” by M. M. P. Muir and R. Threlfall.

“Laboratory Notes :” by M. M. P. Muir.

“On Suberone :” by C. Schorlemmer and R. S. Dale.

“On Isodinaphthylsulphonic Acids and on Phenyl-naphthalene :” by Watson Smith and T. Takamatsu.

“On Dimethylmalonic Acid and Dimethylbarbituric Acid :” by L. T. Thorne.

November 17th, 1881.

Dr. Gilbert, Vice-President, in the Chair.

The following papers were read :—

“Aluminium Alcohols (Part II) : their Products of Decomposition by Heat :” by J. H. Gladstone and A. Tribe.

"On the Chemical Action of decomposing Vegetable Matter on the Rock-forming Sediment of the Carboniferous Period:" by A. Wethered.

"On α - and β -Amylan:" by C. O. Sullivan.

"On the Action of Oxides on Salts (Part IV), Potassic Chlorate, and Ferric Oxide:" by E. J. Mills and G. Donald.

"On the Steeping of Barley:" by E. J. Mills and J. Pettigrew.

December 1st, 1881.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"Researches on the Laws of Substitution in the Naphthalene Series (Part II):" by H. E. Armstrong.

"On Benzylphenol and its Derivatives:" by E. H. Rennie.

"Note on the Action of Ethylchlorocarbonate on Benzene in presence of Aluminium Chloride:" by E. H. Rennie.

"On the Production of Oxalic Acid by Oxidation of Paraffin Oil:" by J. Gallatly and J. S. Thomson.

December 15th, 1881.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

C. Armitage, Dewsbury; J. Bingley, Northampton; C. H. Bothamley, Leeds; J. D. Custance, South Australia; G. W. H. Clements, Bilbao, Spain; E. A. Demarçay, Paris; T. Farmer, Liverpool; A. B. Griffiths, Dulwich; R. P. Gardener, St. John's Wood Park; W. B. Harrington, Cork; H. E. Head, Landore; J. Innes, Llanelly; W. Jackson, Northampton; R. V. Jackson, Glasgow; P. S. Looker, Rhymney, S. Wales; R. F. Mathews, Battersea; K. D. Naegamvale, Malabar Hill, Bombay; J. B. Orr, Eltham, Kent; W. F. Reid, Stowmarket; W. Rupp, New York; H. Ross, Lancaster; F. Sear, Lavender Hill, S.W.; C. H. Sieber, Whitworth; J. W. Stevens, Blandford; C. H. Slaytor, Doncaster; D. N. Steuart, Broxburn, N.B.; B. E. Smith, Wandsworth, S.W.; C. A. Stitt, Dalruth, N.B.; R. Tervet, Johnstone, N.B.; J. S. Topham, Exeter; Rev. E. W. Volckson, Bath; B. Wilkinson, Manchester; J. Whitlock, Lancaster.

The following papers were read:—

"On Some Higher Oxides of Manganese and their Hydrates:" by V. H. Veley.

"On a New Alkaloid from Cinchona Bark:" by D. Howard and J. Hodgkin.

"Contributions to the Chemistry of the Rare Earth-metals:" by B. Brauner.

January 9th, 1882.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

F. Barkas, New Zealand; E. D. Chester, Venezuela; J. Gray, Somerset House, W.C.; H. E. Irons, Enfield; J. P. Laws, St. John's Park, N.; F. H. Lescher, Bartholomew Close, E.C.; D. O. Masson, Edinburgh; H. F. Moore, Hammersmith; T. Perry, Torquay; J. R. Parker, Hackney, E.

The following papers were read:—

"The Chemistry of Bast Fibres:" by C. F. Cross and E. J. Bevan.

"A New Apparatus for Determining Fusing Points:" by C. F. Cross and E. J. Bevan.

"On the Action of Heat on Mercuric Chloride:" by T. Carnelley.

"Contributions to the History of Cerium Compounds:" by W. N. Hartley.

"On the Reaction of Chromic Anhydride with Sulphuric Acid:" by C. F. Cross and A. Higgin.

"On Dibenzylaniline and its Isomerides:" by A. Higgin.

February 2nd, 1882.

Prof. Williamson, Vice-President, in the Chair.

Prof. Odling delivered a Lecture on "The Unit Weight and Mode of Constitution of Compounds."

February 16th, 1882.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

F. J. Alford, Taunton; H. L. Buckeridge, Duke Street, W.; A. Blaikie, Edinburgh; J. J. Beringer, Cornwall; W. E. Bush, Clapton; G. W. Davies, Stockport; J. F. Heyes, Liverpool; W. Hamilton, Madras; T. Isherwood, Blackburn; H. H. Phillips, Manchester;

T. Pitt, Coleman Street, E.C.; H. Porter, Forest Hill, S.E.; G. McRobert, Ardter, Stevenston; C. H. Ridsdale, Stockton-on-Tees; V. O. Sells, Newark-on-Trent; L. T. Thorne, Fortess Road, N.W. S. Young, Bournemouth.

The following papers were read:—

"On Benzyl-phenol and its Derivatives (Part II):" by E. H. Rennie.

"On the Chemical Examination of the Buxton Thermal Water:" by J. C. Thresh.

"On Retrograde Phosphates:" by F. J. Lloyd.

"Contributions to our Knowledge of the Composition of Alloys and Metal Work, for the most part Ancient:" by W. Flight.

"On the Dissociation of Chlorine:" by A. P. Smith and W. B. Lowe.

March 2nd, 1882.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"On the Action of Aldehydes on Phenanthraquinone in Presence of Ammonia (3rd notice):" by F. R. Japp and F. W. Streatfeild.

"Application of the Aldehyde and Ammonia Reaction in Determining the Constitution of Quinones:" by F. R. Japp and F. W. Streatfeild.

"On the Solubility of Glass in certain Reagents:" by R. Cowper.

"Analysis of a Piece of Oxidised Iron from the Condenser of H.M.S. 'Spartan':" by R. Cowper.

"On the Action of Sodium Hydrate and Carbonate on Felspars and Wollastonite:" by W. Flight.

"On the Preparation of Pure Nitrogen:" by W. Flight.

"Some Observations on the Luminous incomplete Combustion of Ether and other Organic Substances:" by W. H. Perkin.

March 16th, 1882.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

H. L. Billing, Plymouth; J. Brown, Dewsbury; H. H. Crawley, Bournemouth; T. Donnelly, Dublin; U. K. Dutt, Montpelier Street, S.W.; W. Fowler, Sunderland; N. Graham, Tulse Hill, S.W.;

A. Hartley, Dulwich, S.E.; A. Hill, Port Glasgow; R. Mar, Brisbane, Queensland; J. T. Smith, Birmingham; F. Vacher, Birkenhead.

The following papers were read:—

“On Valency:” by H. E. Armstrong.

“On the Preparation of Diethylnaphthylamine:” by B. E. Smith.

“On the Action of Sulphuric Acid on Diethylnaphthylamine:” by B. E. Smith.

“On the Action of Phosgene Gas on Diethylnaphthylamine:” by B. E. Smith.

“On some Constituents of Rosin Spirit:” by G. H. Morris.

“Contributions to the Chemical History of the Aromatic Derivatives of Methane:” by R. Meldola.

“On Pentathionic Acid (Part II):” by Watson Smith.

March 30th, 1882. (Annual General Meeting.) See page 229.

April 6th, 1882.

Dr. Gilbert, President, in the Chair.

The following papers were read:—

“On the Action of Acetyl Chloride on Fumaric Acid:” by W. H. Perkin.

“Some Arguments in favour of the Prism Formula of Benzene:” by W. K. Dutt.

“Note on a convenient Apparatus for the Liquefaction of Ammonia:” by J. Emmerson Reynolds.

“On the Transformation of Urea into Cyanamide:” by H. J. H. Fenton.

“On the Action of Haloid Acids upon Hydrocyanic Acid:” by L. Claison and F. E. Matthews.

April 20th, 1882.

Dr. Gilbert, President, in the Chair.

The following papers were read:—

“On the Atomic Volume of Iodine:” by W. Ramsay.

“On the Action of Acetone on Phenanthraquinone both alone and in presence of Ammonia:” by F. R. Japp and F. W. Streatfeild.

"A Study of some of the Earth-metals contained in Samarskite:" by H. E. Roscoe.

"On the Spectrum of Terbium:" by H. E. Roscoe and A. Schuster.

"On the Action of Thiophosphoryl Chloride on Silver Nitrate:" by T. E. Thorpe and S. Dyson.

"On the Behaviour of Zinc, Magnesium, and Iron as Reducing Agents with Acidulated Solutions of Ferric Salts:" by T. E. Thorpe.

"Experiments on the Action of Potassium Amalgam, Sulphuretted Hydrogen, and Potassium Hydrate respectively on Tetra- and Pentathionates of Potassium:" by V. Lewes.

May 4th, 1882.

Dr. Gilbert, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

L. W. Andrews, Springfield, U.S.A.; J. H. Beckett, Manchester; B. A. Burrell, Leeds; J. H. Bicket, Kilmarnock; J. Falkner, Dublin; G. R. Faulkner, Cirencester; W. J. Kemp, Surrey; S. Langdon, Kandy, Ceylon; E. G. Love, New York; A. F. Price, San Francisco; W. H. A. Peake, Stellenbosch, Cape Colony; A. N. Palmer, Wrexham; J. Robinson, Llanfairfechan; S. P. Sadtler, Philadelphia; W. C. Samuel, Herne Hill, S.E.; J. H. Smith, Nottingham; J. H. Stebbins, New York; P. W. Squire, Oxford Street, W.; L. Taylor, Hackney, E.; G. Watson, Glasgow.

Prof. Dewar delivered a lecture "On Recent Developments of the Theory of Dissociation."

May 18th, 1882.

Dr. Gilbert, President, in the Chair.

The following papers were read:—

"On the Precipitation of Alums by Sodie Carbonate:" by E. J. Mills and R. L. Barr.

"On the Rotary Polarisation by Chemical Substances under Magnetic Influence:" by W. H. Perkin.

"On the Constitution of Amarine and Lophine:" by F. R. Japp and H. H. Robinson.

June 1st, 1882.

Dr. Gilbert, President, in the Chair.

The following papers were read:—

- "On the Determination of Nitric Acid in Soils:" by R. Warington.
 "On a Spectroscopic Study of Chlorophyll:" by W. J. Russell and W. Lapraik.

June 15th, 1882.

Dr. Gilbert, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

R. Alexander, New Cross, S.E.; B. Branner, Manchester; J. J. Dobbie, Glasgow; C. J. Ellis, Glasgow; W. L. Goodwin, New Brunswick, Canada; D. E. Johnstone, Southport; T. W. Lowibond, Greenwich, S.E.; R. W. Pullar, Tayside, Perth; R. N. Wolfenden, Welbeck Street, W.

The following papers were read:—

- "Notes on β -Naphthaquinone:" by C. E. Groves.
 "On some New Compounds of Brazilein and Hæmatein:" by J. Hummel and A. G. Perkin.
 "On the Determination of Nitric Acid as Nitric Oxide by Means of its Reaction with Ferrous Salts (Part II):" by R. Warington.
 "On a New Process of Bleaching:" by J. J. Dobbie and J. Hutcheson.

Donations to the Library, 1881-82:—

- "A Treatise on Chemistry." Vol. iii. "Organic Chemistry." Part 1: by Professors Roscoe and Schorlemmer.
 "Practical Chemistry:" by A. Vernon Harcourt, M.A., F.R.S., and H. G. Madan, M.A., F.C.S. Third Edition: from the Authors.
 "Chemical and Physical Researches:" by Josiah Parsons Cooke: from the Author.
 "Handbook of Metric Measures and their English Equivalents:" by W. G. Borns: from the Author.
 "Photography with Emulsions:" by Captain Abney, R.E., F.R.S.: from the Author.
 "Sprengel's Vacuum-pump:" by H. Sprengel: from the Author.
 "Useful Information in Electric Lighting:" by Killingworth Hedges: from the Author.
 "The Scientific Roll and Magazine of Systematised Notes:" conducted by Alexander Ramsay. Climate, Vol. i: from the Editor.
 "Thermometric Scales:" by Dr. T. Stevenson: from the Author.

"Handbook of the Collection of the Wild Silks of India, in the Indian Section of the South Kensington Museum:" by Thomas Wardle: from the Author.

"Water-supply of the City of New York:" by E. Waller, Ph.D.:
from the Author.

"Science and Industry:" an address delivered in the Town Hall, Birmingham, October 20th, 1881: by Dr. C. W. Siemens:
from the Author.

"The Analysis of Phosphates and Method of expressing the Results:" by T. Jamieson: from the Author.

"Ausführliches Lehrbuch der Chemie:" 3ter Band. Organische Chemie. Erste Abtheilung: von H. E. Roscoe, F.R.S., and C. Schorlemmer, F.R.S.: from the Authors.

"Handbuch des krystallographisch-physikalischen Theils der Mineralogie: von C. Rammelsberg: from the Author.

"Premiers Resultats des Études sur la formation des Matières colorantes par voie électrochimique: exposés par F. Goppelsroeder:
from the Author.

Periodicals:—

"Philosophical Transactions for 1881:" from the Royal Society.

"The Chemical Gazette from 1848 to 1859:" from Dr. Francis.

"Annual Reports of the Deputy Master of the Mint." i to xi (1870—1880): from W. Chandler Roberts, Esq.

"Report of the 51st Meeting of the British Association for the Advancement of Science, held at York, 1881:" from the Association.

"Address to the Chemical Section of the British Association at York, 1881, on the Growth of the Atomic Theory:" by Dr. A. W. Williamson, F.R.S.: from the Author.

"Army Medical Department Report for 1879:"
from the Department.

"The Analyst for 1882:" from the Editors.

"The Chemist and Druggist, 1882:" from the Editor.

"The Chemical News, 1881—82:" from the Editor.

"Quarterly Journal of the Geological Society, 1882:"
from the Society.

"Quarterly Journal of Science." Vol. xii: from the Editor.

"Chemical Review, May, 1882:" from the Editor.

"The Dyer and Textile Colourist, June, 1882:" from the Editor.

"Journal of the Society of Arts, 1881—82:" from the Society.

"Journal of the Society of Chemical Industry." No. 1:
from the President.

"Journal of the Iron and Steel Institute, 1882; also 1879, No. 2, and 1881, No. 2:" from the Institute.

- "Mineralogical Magazine, 1882:" from the Mineralogical Society.
- "Pharmaceutical Journal and Transactions, 1881-82:"
from the Pharmaceutical Society.
- "Year-book of Pharmacy, 1881:" from Professor Attfield.
- "Proceedings of the Physical Society of London, 1881:"
from the Society.
- "Catalogue of the Scientific Books in the Library of the Royal Society:" from the Society.
- "Transactions of the Royal Society of Edinburgh." Vol. xxx,
Part I, Session 1880-81.
- "Proceedings of the same (1880-81):" from the Society.
- "Proceedings of the Philosophical Society of Glasgow, 1880-81:"
Vol. xiii, No. 1: from the Society.
- "The Glasgow University Calendar for 1881-82:"
from the University.
- "Reports of the Mitchell Library, Glasgow, 1880 and 1881:"
from the Librarian.
- "Easter Ardross Experimental Station Report for 1880-81:"
J. McDonald Cameron: from the Author.
- "Geological Survey of Canada (1879-1880):"
from the Director.
- "Transactions of the South African Philosophical Society." Vols. i
and ii (1878-1880): from the Society.
- "Journal and Proceedings of the Royal Society of New South
Wales, 1880-81 and 1881-82:" from Prof. Liversidge.
- "Report of the School of Mines, Ballarat." Presented at the
Meeting of Governors, May 24th, 1882: from the Reporter.
- "American Chemical Journal:" edited by Ira Remsen. Vol. iv,
Nos. 1, 2, and 3: from the Editor.
- "American Journal of Science and Arts." Vols. xxiii and xxiv:
from the Editors.
- "Proceedings of the American Philosophical Society, January to
December, 1881:" from the Society.
- "Annual Report of the Commissioner of Agriculture (U.S.) for
1880:" from the Department of Agriculture.
- "Abhandlungen der Königl.-baeyrischen Akademie der Wissen-
schaften." Bd. xiv. Erste Abtheilung:
from the Royal Bavarian Academy.
- "Denkschriften der Kaiserlichen Akademie zu Wien (Mathemat.-
naturw. Klasse)." 41ter Band: from the Academy.
- "Sitzungsberichte derselben:" 82ter Band: from the Academy.
- "Sitzungsberichte der Königlich-preussischen Akademie der Wis-
sensschaften zu Berlin, i-xvii, 1882: from the Academy.

"Oversigt over det Kongelige Danske Videnskabernes Selskabs Förländlingar og des Medlemmers Arbeeten, 1880-81 :"

from the Royal Danish Academy of Sciences.

"Kongliga Svenska Vetenskaps Akademiens Handlingar." Bd. xiv-xvii (1876-1878) :

from the Royal Swedish Academy of Sciences.

"Kongliga Svenska Vetenskaps Akademiens Förländlingar, 1877-1880 : " from the Royal Swedish Academy of Sciences.

"Meddelser fra Carlsberg Laboratoriet Andet Hefte, 1879 : "

from the Royal Danish Academy of Sciences.

"Verhandlungen der Kaiserl-Leopold Carolinischen Deutschen Akademie der Naturforscher." xxi Band, 2te Abtheilung, 1880 :

from the Academy.

"Verhandlungen und Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Würzburg, 1881 : " from the Society.

"Vierteljahresschrift der naturforschenden Gesellschaft in Zürich, 1880 and 1881 : " from the Society.

"Comptes rendus des Séances et Mémoires de la Société de Biologie." 6me Série, Tomes 5 et 6, 7me Série, tome 1, 1880 :

from the Society.

"Bulletin de l'Académie Royale des Sciences de Belgique, 1881-82."

"Annuaire de l'Académie Royale des Sciences de Belgique, 1881-82 : " from the Academy.

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